POLYURETHANE DISPERSIONS FOR PAPER COATINGS

By

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DECLARATION

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree.

POLYURETHANE DISPERSIONS FOR PAPER COATINGS

ABSTRACT

Aqueous polyurethane (PU) dispersions were synthesized for the use in paper coatings. These PUs contained a polyester polyol soft segment (content of 60-70%) and a urethane hard segment (content of 30-40%). This was followed by grafting using four different grafting agents. Triethylamine (TEA) was used as the neutralizing agent. The polyester polyol segment consisted of neopentyl glycol (NPG), adipic acid, 1,4-cyclohexane dicarboxylic acid (1,4-CHDCA) and 2-phosphonobutane-1,2,4- tricarboxylic acid (PBTCA), while the urethane hard segment consisted of hydrogenated 4,4-diphenylmethane diisocyanate, dimethylolproponic acid (DMPA), 3-hydroxypivalic acid (HPA) and hydroxyethylene methacrylate (HEMA). The grafting agents used were lauryl methacrylate (LMA), n-butyl methacrylate (n-BMA), methyl methacrylate (MMA) and styrene.

Two different polyester polyols were synthesized, one containing 10% phosphate and the other none. The polyols were characterized in terms of their acid value, hydroxyl value and molecular mass. The PUs synthesized from the polyol containing 0% phosphate were grafted with LMA, while the phosphate-containing PUs were grafted with each of the all four grafting agents.

The resulting dispersions were applied to paperboard, and then dried at a maximum temperature of 100°C. The PU-coated paperboard was characterized using the moisture vapour transmission rate (MVTR), and scanning electron microscopy (SEM) techniques.

PU films (not supported by paper, stand alone) were prepared by heating the PU dispersion in Teflon holders up to 130°C for 6 hours. The dried films were then characterized by thermogravimatric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and Fourier transform infrared spectroscopy (FTIR).

MVTR-analysis showed that the phosphated PU coatings had a minimum MVTR-value at 0% grafting, and that its overall MVTR-values were much lower than that of the non-phosphated PU coatings. SEM-analysis showed that the phosphated PU coatings had no pinholes at a maximum of 8% grafting, while the non-phosphated PU coatings showed pinholes at all levels of grafting. DMA-analysis showed that the phosphated PU samples had higher T_g's (T_g onset between 0-5°C) than that of the non-phosphated PU samples (T_g onset below –50°C).

POLI-URETAAN DISPERSIES VIR PAPIER BEDEKKINGS

OPSOMMING

Waterige poli-uretaan (PU) dispersies is gesintetiseer vir gebruik as papierbedekkings. Hierdie poli-uretane het 'n poliester poli-ol sagte segment (60-70% inhoud) en 'n uretaan harde segment (30-40% inhoud) bevat. Die poli-uretane is met vier verskillende ent-middels geëent. Trietielamien (TEA) is as neutraliseermiddel gebruik. Die poli-ester poli-ol segment het bestaan uit: neopentielglikol (NPG), adipiensuur, 1,4-sikloheksaandikarboksielssuur (1,4-SHDKS) en 2-fosfonobutaan-1,2,4-trikarboksielssuur (FBTKS). Die uretaan harde segment het bestaan uit: hidrogeneerde 4,4-difenielmetaandiisosianaat, dimetielpropioonsuur (DMPS), 3-hidroksipivaalsuur (HPS) en hidroksietileenmetakrilaat (HEMA). Laurielmetakrilaat (LMA), n-butielmetakrilaat (n-BMA), metielmetakrilaat (MMA) en stireen is as entmiddels gebruik.

Twee verskillende poli-ester polihidroksie verbindings is gesintetiseer: een met 10% fosfaat en een met geen fosfaat, en gekarakteriseer in terme van hulle suurwaardes, hidroksiwaardes en molekulêre massas. The PUs wat vanaf die fosfaat-bevattende poli-ol gesintetiseer is, is met LMA geëent, terwyl die fosfaat-bevattende PUs met al vier entmiddels geëent is. Papier (Eng. paperboard) is met hierdie dispersies bedek en by 100 °C gedroog. Die PU-bedekte papier is gekarakteriseer in terme van vogdeurlaatbaarheidstransmissie (Eng: MVTR – the moisture vapour transmission rate), en skandeerelektonmikroskopie (SEM).

PU-films wat nie deur papier gestut is nie is ook voorberei deur die verhitting van die PU dispersies in Teflon houers (130 °C, 6 ure). Die droë films is daarna gekarakteriseer deur middel van termogravimetriese analise (TGA), differensiële skandeerkalorimetrie (DSC), dinamiese meganiese analise (DMA) en Fourier-transformasie infrarooispektroskopie (FTIR).

Resultate van MVTR analises het getoon dat die fosfaat-bevattende PU bedekkings 'n mimimum MVTR-waarde by 0% enting gehad het, en dat die totale MVTR waardes baie laer was as die van die nie-fosfaatbevattende bedekkings. SEM het gewys dat die fosfaat-PU bedekkings by 8% enting geen mikrogaatjies (Eng. pinholes) gehad net nie, terwyl die PU bedekings met geen fosfaat mikrogaatjies (Eng. pinholes) by alle vlakke van enting gehad het. DMA analises het getoon dat die monsters van die fosfaatbevattende PU hoër Tg waardes gehad het (Tg begin tussen 0 en 5 °C) as die nie-fosfaatbevattende PU monsters (Tg begin onder -50 °C).

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

ABBREVIATIONS

CHDCA	1,4-Cyclohexane dicarboxylic acid
DCA	Dynamic Contact Angle
DMA	Dynamic Mechanical Analysis
DMPA	Dimethylolproponic acid
DSC	Differential Scanning Calorimetry
E/VA	Ethylene-vinyl acetate copolymer
FTIR	Fourier Transform Infrared Spectroscopy
H_{12}MDI	Hydrogenated 4,4-diphenylmethane diisocyanate
HDI	1,6-hexamethylene diisocyanate
HCl	Hydrochloric acid
HEMA	Hydroxyethylene methacrylate
HPA	3-Hydroxypivalic acid
LMA	Lauryl methacrylate
MDI	4,4-diphenylmethane diisocyanate
MF	Melamine formaldehyde
MMA	Methyl methacrylate
MVTR	Moisture vapour transmission rate
NaCl	Sodium chloride
n-BMA	n-Butyl methacrylate
NPG	Neopentyl glycol
PBTCA	2-Phosphonobutane-1,2,4- tricarboxylic acid
PE	Polyethylene
PEI	Polyethyleneimide
PP	Polypropylene
PVA	Polyvinyl acrylate
PVAc	Polyvinyl acetate
PVDC	Polyvinylidene chloride
PVOH or PVAl	Polyvinyl alcohol
RH	Relative humidity
SEM	Scanning Electron Microscopy
TDI	Toluene diisocyanate
TEA	Triethylamine
T_g	Glass transition temperature
TGA	Thermogravimetric Analysis
UF	Urea formaldehyde

1 INTRODUCTION

1.1 Introduction

The development of environmentally friendly coatings from conventional solvent-borne systems has been going on for more than 20 years. Solvent-borne systems are being replaced by the development of high solid coatings, powder coatings, and water-borne coatings. The latter are preferred due to their compatibility with conventional coating systems.

Water-borne coatings are produced by emulsion polymerization. They include acrylics, polyester and polyurethane dispersions. Water-borne polyurethane systems combine low volatility content properties with the good film properties of solvent-borne systems, along with the inherent properties of the urethanes.

Various homo- and copolymers are currently used as coatings for paperboard (See section 2.4.1). Amongst the desired properties, the following are very important:

- Blocking resistance
- Low moisture vapour transmission rate (MVTR)
- Easy processability and coatability
- Environmentally friendliness
- Recyclability of coated paperboard
- Non-toxicity for food application
- Low T_g (about –15°C) for crack resistance at low temperatures
- Low cost

Currently, PVDC coatings exhibit the lowest MVTR-values when tested under tropical conditions, i.e. 38°C and 90% RH. There is however several disadvantages associated with the use of this type of coating. These include the actual coating process, which requires two coats, and very careful drying conditions[1]. Hydrochloric acid (HCl) is released during the burning of the PVDC coating, which is environmentally unfriendly, and its usage in cold temperatures is not recommended, due to the polymer's brittleness at these cold conditions.

Hot-melts, such as PE, are used for cold food packaging. Their major problem is that the coating makes the paperboard non-recyclable.

Other coatings currently being used, do not comply with all of the above requirements. The main objective of this study was therefore to produce a coating for Dry Food Packaging that meets all the above requirements. As polyurethanes can be tailor-made to specific specifications, their application as a coating for paperboard, for use in the packaging industry can be extremely versatile.

1.2 Objectives

The specific objectives of this study are the following:

I. Synthesis of a hydrophobic polyol.
II. Synthesis of a stable polyurethane with ionic groups for self-dispersibility to form a stable polyurethane dispersion..
III. Modification of polyurethane with acrylic polymer grafts.
IV. Investigating the effect of phosphorous containing monomer on the coating properties.
V. Investigating the effect of the different grafting agents, which include lauryl methacrylate (LMA), methyl methacrylate (MMA), n-butyl methacrylate (n-BMA) and styrene on MVTR-values.
VI. Investigating the effect of the addition of wax emulsions containing functionalized and unfunctionalized wax polymers on the characteristics of the PU/wax composites.
VII. Fully characterising the polyurethane coating using DSC, DMA, FTIR, MVTR and SEM.

1.3 References

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2 PAPERBOARD

2.1 Terminology

Paper is generally termed board (or paperboard) when its substance is greater than 220g/m^2. The term paperboard usually signifies that the paper material has a heavier basis weight than paper as such, and that it is likely to be more rigid and thicker. *Paperboard* is usually classed as such when its thickness exceeds 0,30mm (0,012 in). One exception is found in the United Kingdom, which uses a lower limit of 0,25mm (0.010 in)[1,2].

Board or paperboard has many terminologies due to different end-usages (See Table 2.1).

Table 2.1: Paperboard terminology [1-4]

Terminology	Description
Container board	This is used for corrugated and solid fiberboard boxes.
Boxboard	This term applies to folding cartons, which can be further divided into: • Folding boxboard • Special food board • Setup (rigid) boxboard
Strawboard	This consist of straw semichemical pulp, which is mainly used for rigid boxes, book covers, picture mountings, etc.
Wood pulpboard	This consists of groundwood pulp, which is used for containerboard, shoe board, and making traveling cases.
Leatherpulp board	This contains at least 50% leather, which is used for boots, shoes and cases.
Resin board	The board is stocked with a thermoplastic resin, which is used for forming and insulation purposes.
Printer's board	Examples include art board, ivory board and bristol board.

2.2 Grades of Paperboard

Paperboard grades include Kraft and recycled paperboard, which can be applied to both the packaging and building industries.

2.2.1 Kraft paperboard

Kraft paperboard is used in the packaging industry and includes two types: *bleached* and *unbleached* paperboard, of which about half of the bleached paperboard is coated. It is used in folding milk cartons, index cards, cups, and plates.

Unbleached paperboard is used in linerboard and corrugated medium for the production of corrugated boxes. Recycled fiber is increasingly being used in unbleached paperboard production.

Linerboard is a two-ply (duplex) sheet, or even triplex sheet, made on a flat wire paper machine with two headboxes. The linerboard is the two outer visible layers covering (or sandwiching) the inner corrugated medium of the corrugated boxes.

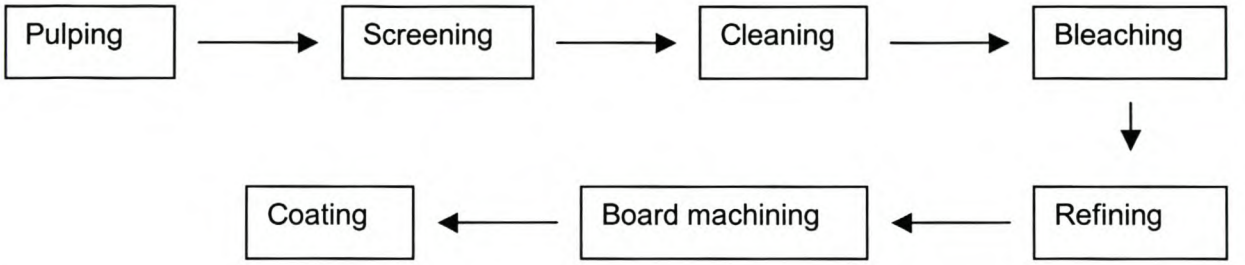
2.2.2 Recycled paperboard

Recycled paperboard is made from waste papers and other inexpensive pulps, of which 90 to 94% is recycled paper and the rest virgin stock. About 80% of all waste paper comes from corrugated boxes, newspapers and office papers. It is very important to keep the different paper sources “pure”. This implies that newspapers should not be mixed with brown paper, magazines and boxes, or office papers with newspaper and brown paper, as this decreases the value of the waste paper.

Grades of recycled paperboard include gypsum (calcium sulphate) liner, core (tube) stock, and clay-coated folding boxboard, which is used in roofing felt, fiberboard, shoe and cereal boxes, etc. These grades have a grayish cast because the furnish (i.e. a combination of all the materials used to make paper) is not de-inked.

2.3 Waste Paper Recycling Process

The main processes[1-9] in the waste paper recycling process can be summarized as follows:



These processes will be discussed in greater detail below.

2.3.1 Pulping process

The pulping process takes place in a pulper, which acts as a large blender that disperses the paper pulp into an aqueous slurry. The pulper consists of a hydrapulper, ragger rope and a junk remover (See Figure 2.1 below).

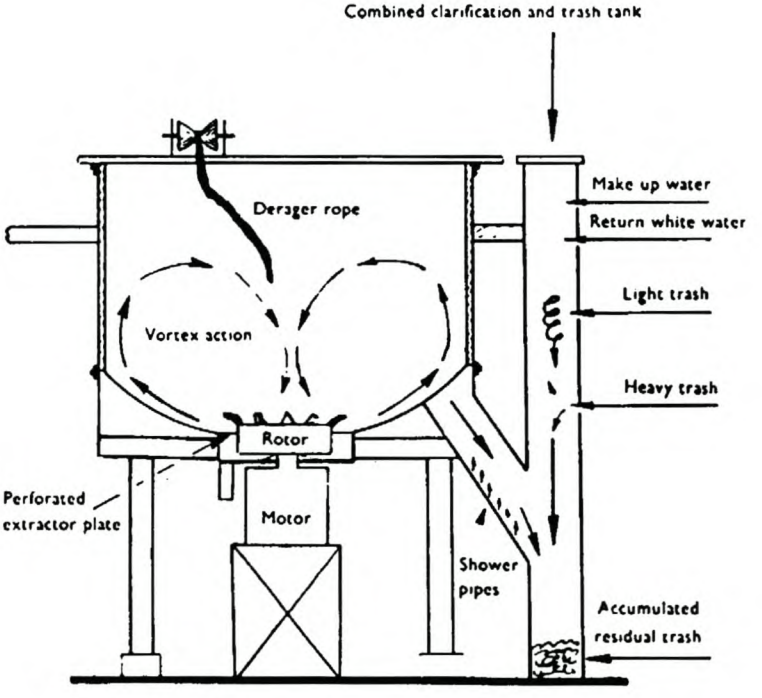


Figure 2.1: Hydrapulper for continuous slushing of waste paper[7]

The ragger is a chain that dangles in the pulper vortex, which is then pulled out slowly over a long period of time. The ragger "collects" waste in the form of baling wire, wires, plastic sheeting, stringy materials, wet strength paper, tapes and other material that wrap around it

as the paper stock rotates in the pulper. The accumulated material forms a rag rope, which is removed and cut (See Figure 2.2).

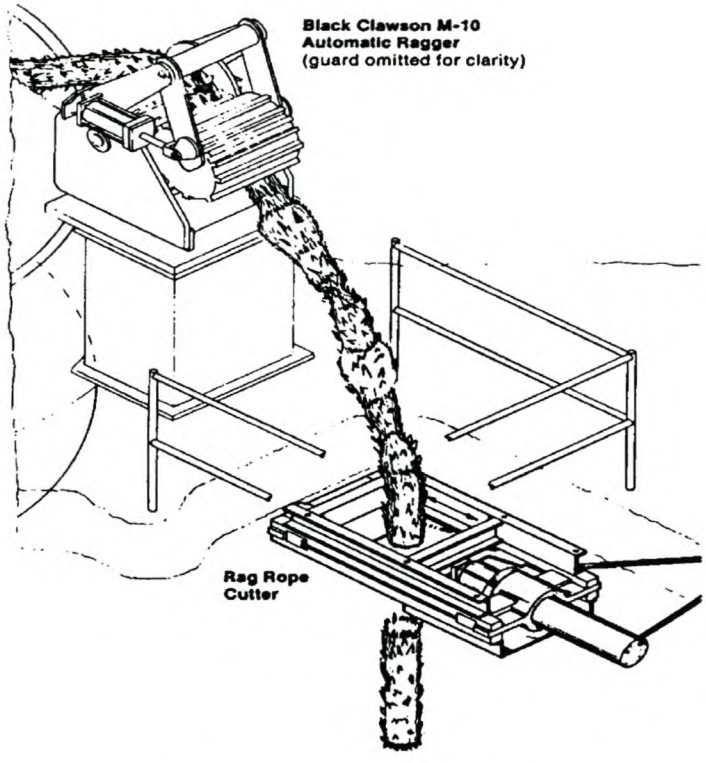


Figure 2.2: Rag rope cutter

Heavy contaminants like nuts, bolts, rock and pipefittings are removed as junk via the junk remover. Thereafter, de-inking occurs in the pulper, typically at 40-70°C and at pH 9-11, depending on the quality and end-use of the pulp. Hydrapulpers, like the Vokes rotor, rotate above a stationary perforated bedplate (See Figure 2.3). The Vokes rotor, in conjunction with the bedplate, permits continuous pulp extraction from the pulper.

Figure 2.3: Vokes rotor with extended bedplate[7]

Pulp from the pulper is mixed with water, and then goes to pressure screens and centrifugal cleaners.

2.3.2 Screening process

The screening process involves the removal of dirt, sand and other large particles from the pulp through small holes or slots, called pressure screens.

2.3.3 Cleaning process

The cleaning process takes place in 3 steps. Firstly, heavy particles are removed from the stock via centrifugal cleaners. Stock enters the cylinder tangentially from the side near the top, causing a vortex to form. Clean stock is removed from the top, while contaminated stock is removed at the bottom.

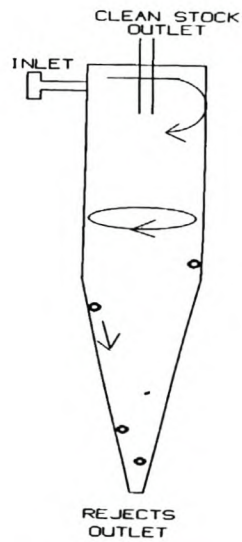


Figure 2.4: Centrifugal Cleaners[6]

Thereafter, lightweight (lighter-than-water) contaminants such as tacky material, pitch, plastics and other polymers are removed via the same principal as the centrifugal cleaners, except that the stock is removed at the bottom, while the contaminants are removed from the top.

2.3.4 Slurry concentration

Finally, after de-inking and cleaning, the dilute pulp mixture (slurry) is concentrated for further processing and storage.

2.3.5 Bleaching process

Bleaching agents are added to increase the whiteness of the final product. Bleaching agents are sometimes added to the pulper to help with ink removal, but they are more efficient when added after the pulp is cleaned and screened.

2.3.6 Refining process

The process of refining or beating is to make wet fiber ready for the board machine. The objective is to increase the area available between fibers to allow for maximum free imbibitions of water as a plasticizer. This increases fiber flexibility so that the fibers can easily deform under surface tension during drying. A desirable effect of refining is to obtain maximum entanglements of the fibers, which thereby significantly increases the sheet strength.

2.3.7 Board machining process

The board machining process takes place where the sheet is built layer by layer, then pressed and rolled until the desired board thickness is reached. From here the sheets pass through drying tunnels, after which they pass through two or three sets of heavy rollers (calendered) to give a smoothing and flattening action. The first calender stack after drying is called the wet stack, and the second set is called the dry stack. Water, starch solutions, etc., are normally applied to the paperboard on the wet stack to improve smoothness and to impart properties such as water resistance, oil resistance, scuff resistance, flame proofing, etc.

2.4 Coating Process

Surface coatings are normally applied to paperboard to impart specific characteristics[8,9]. There are two types of coatings, namely printable clay-type coatings and functional coatings.

Specific reasons for using printable clay-type coatings on paperboard include:

- To improve surface receptivity to ink
- To mask original surface characteristics
- To reduce abrasion and fiber fluffing (picking) during printing
- To upgrade the texture of the paperboard
- To increase the attractiveness and sales value of the paperboard

Functional coatings impart *barrier-type* properties and/or *physical (material)-type* properties (See Table 2.2). It is normally applied to the opposite side of the printable pigmented coatings, but they can also be applied to both sides.

Table 2.2: Properties of paperboard with functional coatings

Barrier-type properties	Physical (material)-type properties
Grease resistance	Slip
Water resistance	Anti-slip
Water vapour resistance	Non-abrasion
Gas permeation resistance	Abrasion or scuff resistance
	Release
	Block resistance
	Heat sealability
	High gloss, clarity, etc.

To ensure the required properties of the coated paperboard, it is imperative that the uncoated paperboard exhibits specific characteristics. These characteristics include:

- Uniformity of formation
- Uniformity of finish, grammage and thickness
- Good dimensional stability with moisture content of ± 7-8%, to ensure a level and curl free sheet

2.4.1 Typical polymers

The most common resins used in paperboard coating include:

- Polyvinyl alcohol (PVOH or PVAl)
- Starch and casein
- Polyvinyl acrylate
- Styrene and butadiene
- Polyvinylidene chloride (PVDC)
- Polyvinyl acetate (PVAc)
- Polyethylene (PE) and polypropylene (PP)

Each of the above resins has their own inherent characteristic properties. On their own, they lack some of the characteristic properties needed to make the ideal coating for a specific application. They are usually modified via copolymerisation to enhance certain properties

and characteristics of the coatings to better suit its end-use. Thus a typical coating will contain at least a combination of the above resins and other copolymers and additives.

PVOH provides strong durable coatings with good optical properties, and the films are completely resistant to almost all organic solvents, oils and greases. PVOH emulsions have low viscosities with high solids contents. The smoothness of the PVOH coatings also allows for greater ease of clay platelet flow under calender loads. When used with starch and casein, some properties are improved, such as better ink holdout, increased gloss, better water resistance and increased flexibility[8,10,11].

Starch is predominantly used to lower the coating cost. The modified starches particularly, are used in a wide range of applications for paper coating, where for example water resistance is a major requirement. Starch can also be crosslinked using glyoxal or urea to impart waterproofing properties[8].

Casein is a globular, amphoteric phosphoprotein that is commercially obtained from cow's milk. It forms a tough film, and when treated with formaldehyde it increases the coating's water resistance. Casein was initially used in the halftone printing process, but it is now also used in high quality coatings for offset printing, where desired surface properties include toughness, water resistance and high gloss[8,12].

Acrylics have a low residual odor, which is why acrylic-coatings are commonly used on paperboard for food packaging. Typical properties of acrylics include high gloss and good ink holdout, which increases print quality. They also have excellent heat, light and chemical resistance, but they are relatively expensive coatings[2,11].

PVAc responds well to calendaring operations to produce a glossy surface, and also provides good heat-sealability, grease and moisture resistance[8]. Copolymers of vinyl acetate and vinyl chloride are used for improved grease resistance coatings[11].

Polybutadiene and *Styrene-butadiene* latexes are mainly used to increase coating strength, and also as a pigment binder. The latex contributes smoothness, gloss, wet-rub resistance, flexibility and gloss ink holdout to many grades of coated paper and paperboard. Butadiene-styrene copolymers are also used for water vapour resistant heat-sealable coatings[2,8,11].

PVDC emulsions provide coating systems with high solids content, minimum viscosity and excellent barrier properties. Vinylidene chloride is normally copolymerised with vinyl chloride

or vinyl acrylate. This results in a coating with excellent barrier properties to moisture vapour, gas, grease, etc. It is also very suitable for printing on. It is mainly used in cartons for dry foods, where the important function is to prevent moisture entering into the carton. PVDC, however, requires two coats, that are often pre-coated with a PVC coating[7]. Process conditions including careful after-drying. The fusion temperature is also very important. Other copolymers include acrylates such as butadiene sulfone-acrylate, methylacrylate, butyl methacrylate and methacrylonitrile-methyl methacrylate[2,8].

Medium density PE is normally used on frozen food cartons. It has good strength, shock resistance and water vapour resistance, but poor grease resistance[2,7].

Paraffin wax is one of the oldest moisture protective coatings[7]. The advantages of paraffin waxes include: cheapness, easy application, simultaneous coating of both sides, and coating at high speeds. Disadvantages include brittleness (flaking of coated board) and adhesive difficulty.

Microcrystalline wax is a good laminating material that gives high barrier properties. By adding rubber-type polymers, the adhesive properties are also increased. This makes the use of microcrystalline wax suitable for laminating chipboard to a variety of lining papers at high speed[7].

Hot melts cover a blend of thermoplastic resins and wax-extended copolymers, such as ethylene-vinyl acetate (E/VA) and ethylene-ethyl acrylate copolymer/wax systems. They are used to coat fiberboard containers and folding cartons, for protective cartons and wet foods, such as fruit, vegetables, fish, poultry, etc[7,8].

2.5 Wet-end adhesives

Wet-end adhesives are natural (e.g. gums and starches) and synthetic (e.g. N-containing) chemicals that are distributed throughout the fiber suspensions during the board machining process, prior to the formation of webs. Advantages of the use of wet-end adhesives include:

- they bond additives and other compounds to the fiber
- they increase burst or tensile strength
- they keep surface fibers together to prevent linting, which causes defective printing.
- they can decrease drying times, thereby increasing production

The mechanism of the wet strength additive can be illustrated by means of an ion exchange between cellulose and the cationic resins:

$$[\text{cellulose-COO}]^-\text{metal}^+ + [\text{resin } NR_2H]^+X^- \longleftrightarrow [\text{cellulose-COO}]^-[NR_2H \text{ resin}]^+ + \text{metal}^+ \text{ and } X^-$$

2.5.1 Wet-end adhesives for wet strength

These thermosetting resins are added to the stock to impart wet strength to the paper or board. Commonly used cationic resins include urea formaldehyde (UF), melamine formaldehyde (MF), polyethyleneimide (PEI), and polyamide amine epichlorohydrin[3,7,13]. UF is the traditional wet strength resin, but has been largely replaced by MF due to the health aspects of formaldehyde emission.

Cationic PEI is retained on cellulose by carboxyl groups, which bind acid dyestuffs and also retain fillers like TiO_2 and $CaCO_3$ effectively. PEI has, however, been replaced by a more effective cationic polyamide amine epichlorohydrin.

2.5.2 Wet-end adhesives for dry Strength

Polyacrylamide is used for heavy paper or paperboard to increase its dry strength, by hydrogen bonding. It must be added after the final refining stage, when alum is well distributed. Pure polyacrylamide is not an effective bonding agent due to poor retention under wet-end conditions. It needs carboxyl groups (COOH) from acrylic acid (about 10%),

and aluminum dimer [$Al(OH)^{+2}$] to accomplish effective retention. For dry strength, the molecular weight of the polyacrylamide is controlled to about 250,000 – 500,000.

Starch is used as a dry-strength agent, drainage aid, retention aid, coating binder and adhesive in corrugated board, etc. Starch is reacted with amine containing materials such as $RCH_2OCH_2CH(OH)CH_2\text{-}N(CH_3)_3^+$ to introduce cationic groups. Anionic and ampholytic (cationic and anionic) starches are also available. Potato starch contains about 0.1% phosphorous, and imparts a slight negative charge due to the phosphate groups.

Guar gum, methyl cellulose, carboxymethyl cellulose, etc. tend to be more expensive, but can also be used as a dry-strength agents.

2.5.3 Conclusions

Although the overall surface charge of the paperboard is anionic, these wet-end adhesives cover the paperboard's surface with long chains containing amine groups, which can also be very good for the adhesion of a polyurethane coating.

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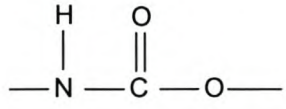
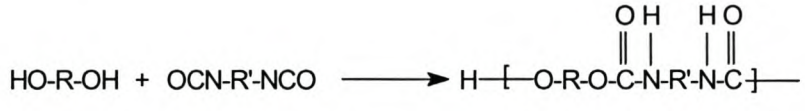
3 URETHANES

3.1 Introduction

The term "urethane" is derived from ethyl carbamate, which is also known as urethane. Polyurethanes (PU) are polymers containing significant number of urethane groups in the molecular chain, which is characterized by the following linkage:



PU can be prepared by a number of methods although the most common method of preparing polyurethanes is condensation reaction of a diisocyanate and a polyol. Unlike conventional polycondensation, this polymerisation reaction does not eliminate any by-product.



Branched or crosslinked PUs are produced when the functionality of either or both components are increased to 3 or more.

By altering the R and R' groups, we can change the properties of the PU (such as molecular weight, degree of crosslinking, effective intermolecular forces, chain stiffness and crystallinity), to better suit its end use. This makes PUs one of the most versatile polymers, which includes fibers, flexible and rigid foams, soft and hard elastomers, coatings and adhesives, and thermoplastic and thermosetting plastics.

3.2 Historical

During the 1940s, PU coatings were among the earliest of PU products to be investigated. In Germany, Bayer and co-workers[1,2] developed polyester-diisocyanate coatings which were suitable for wood, rubber, leather, fabrics, paper and metals. They found that a wide variety of properties were obtained when they varied the type and degree of branching of the polyester and diisocyanate, as well as the NCO/OH ratio.

These coatings had several outstanding characteristics including high gloss, good adhesion to many substrates, high abrasion resistance, excellent electrical properties, good weather resistance, and excellent water, oil, and solvent resistance.

During the Second World War, PU coatings were used to impregnate paper for the manufacture of mustard gas-resistant garments[1]. They were also used in anticorrosion paints in chemical plants and high-gloss finishes on aeroplanes. Pigmented coatings were especially used for metal, wood and masonry protection.

PU coatings are made via a one- or two-component system. One-component coatings consist of blocked isocyanates and polyols, which have found commercial use as wire enamels. In two-component coatings the hydroxyl-group of the polyester reacts with the isocyanate groups, where the NCO/OH ratio >1, to form excess isocyanate groups, which can than react further with moisture to form urea groups as well.

Another kind of urethane coating, termed “urethane oils”, was also reported by Bayer, followed by extensive studies by the Americans and British for relative low-cost coatings[1,3,4,5]. It was made by reacting diisocyanate with the alcoholysis product of a drying oil, e.g., mono or diglycerides from linseed oil. These products did not contain free NCO-groups, which made them stable on storage and they could be readily pigmented. Drying occurs via the double bond of the fatty acid part of the molecule. These coatings exhibit superior properties to alkyd resins with regard to curing speed, hardness, and water resistance. In 1960 the United States used the largest volume of urethane coatings synthesized by such systems[6].

Urethane coatings based on castor oil-diisocyanate adducts have also been reported[7,8.9.10]. They have found commercial acceptance for use in concrete floors, in maintenance and protective coatings, and other applications which require good weather, abrasion and chemical resistance.

Polyether-based coatings via one- and two-component systems[2,12,13,14], are recommended for use as leather and wood finishes, concrete coatings, and metal finishes for corrosion protection.

3.3 Polyurethane Dispersions

In the 1970's, increasing environmental legislation was imposed to limit volatile organic solvent emissions into the atmosphere. Research into more user-friendly (or solvent-free) coatings lead to the development of water dispersible ionic urethanes. A major problem in the development in aqueous PUs was poor commercial competitiveness compared to that of solvent-based PU systems. The synthesis and characterization of PU dispersions are well described in the literature[15-29]. PU dispersions have received considerable attention due to their usefulness in coatings[30].

Ionic groups are frequently introduced into PU dispersions by monomers or chain extenders containing tertiary amine groups, and pendent sulfonic or carboxylic acid groups. These acid groups are subsequently neutralized with various cations to produce anionomers, which can then be dispersed into water.

3.4 Types of Polyurethane Dispersions

There are various types of PU dispersions, based on its ionic character. These types include non-ionic, cationic and anionic polyurethane dispersions.

3.4.1 Non-ionic Polyurethane dispersions

Non-ionic PU dispersions include PU dispersions with a hydrophilic monomer, such as polyesters derived from ethylene and propylene oxide. Advantages offered by these polyesters include mechanical and storage stabilities, while disadvantages include their susceptibility to water damage due to their inherent hydrophilicity[31].

3.4.2 Cationic Polyurethane dispersions

These dispersions are prepared by incorporating monomers containing tertiary amine groups such as n-methyl diethanolamine into the PU. The tertiary amine may be quaternized by an alkylating agent, aryl halides, or with an acid. Properties and synthesis mechanisms have been reported in the literature[32-35].

3.4.3 Anionic Polyurethane dispersions

Anionic PU dispersions are mainly prepared by introducing ionic groups during addition polymerization or by post-polymer modification techniques. Ionic groups including sulfonic, carboxylate and phosphoric acid groups, bring about significant changes in the properties of PU[15,30,36-48], transforming PUs that are generally waterproof in nature to water-wetting or even water-soluble ones.

A versatile and effective way of controlling the ionic content on the polymer backbone is by the introduction of ionic groups, using ionic diols such as dimethylol propionic acid (DMPA). Here the two primary hydroxyl groups react with the isocyanate, while the tertiary carboxylic acid is very unreactive due to steric hindrance. These pendent carboxylic acid groups are neutralized by means of a suitable base to generate the ionic centers.

3.5 Raw Materials

Urethanes can be synthesised from various monomers. The most widely method, however, consisted of the following two components:

- Isocyanate component
- Hydroxyl component

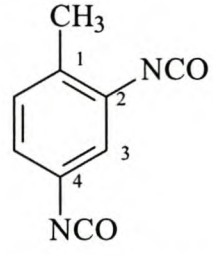
These components will be discussed in greater detail below.

3.5.1 Isocyanate components

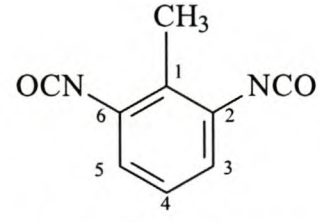
The isocyanate component can either have an aromatic or aliphatic character.

3.5.1.1 Aromatic isocyanates

The most commonly used aromatic isocyanates are toluene diisocyanate (TDI) and 4,4-diphenylmethane diisocyanate (MDI), and some modifications of these products (See Figure 3.1 and 3.2 below).



2,4-toluene diisocyanate

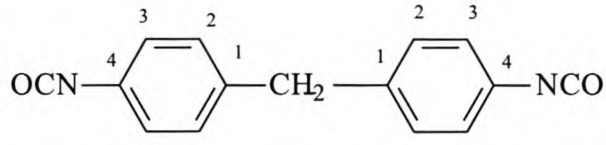


2,6-toluene diisocyanate

Figure 3.1: TDI Isomers

TDI is a colorless liquid with a boiling point of 120°C at 10mm Hg and is normally found in a blend of 80:20 in terms of the 2,4- and 2,6- isomers.

Temperature has a big influence on the reactivity of the NCO groups in their various ortho- and para- positions. At 25°C, the NCO group in the para position is eight to ten times more reactive than the NCO group in the ortho position. As the temperature increases, the reactivity of the ortho NCO group increases at a far greater rate than that of the para NCO group, until their reactivities are equal at 100°C. The difference in activity at low temperature allows for polymer synthesis with an "ordered arrangement". TDI is used in the production of flexible foams, coatings, sealants, elastomers, adhesives, and other applications[49].



4,4-diphenylmethane diisocyante

Figure 3.2: 4,4-diphenylmethane diisocyante (MDI)

MDI is a solid with a melting point of 37°C. It contains two equally reactive NCO groups. MDI tends to dimerize at room temperature. It should therefore be stored below 0°C as a solid, or between 40-50°C as a liquid, to minimize dimerization. MDI is used in the production of rigid foams, elastomers, some coatings, and spandex-fiber applications.

3.5.1.2 Aliphatic isocyanates

The first commercially used aliphatic diisocyanate was 1,6-hexamethylene diisocyanate (HDI). It is a colorless liquid that boils at 127°C at 10mm Hg and is less reactive than TDI and MDI. The reactivity is however increased by metal catalysts, such as tin or tertiary amines to equal or better the NCO reactivity in TDI[50]. HDI provides better resistance to discoloration, hydrolysis and heat degradation than TDI.

More recently commercially available aliphatic diisocyanates include "dimeryl" diisocyanate and hydrogenated MDI (H_{12}MDI)[51]. These diisocyanates give excellent color stability to urethane and urea coatings. Others include hydrogenated TDI (H_6TDI) or cyclohexyl diisocyanate, isophorone diisocyanate[52] and lysine diisocyanate[53].

3.5.2 Hydroxyl Components

Hydroxyl components normally used include hydroxyl-terminated polyesters and polyethers.

3.5.2.1 Hydroxyl-terminated polyesters

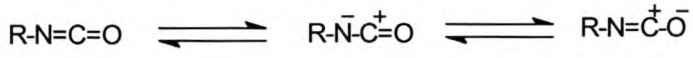
These polyesters are extensively used for elastomers, coatings and spandex fibers. Components mostly used include adipic acid, phthalic anhydride, dimerized linoleic acid, monomeric glycols and triols[52]. Polyesters containing aromatic components, such as phthalic anhydride, impart higher temperature resistance and chain rigidity. Castor oil and its derivatives are an important class of polyesters for coatings. Their presence in polyurethanes gives excellent water resistance and good weather resistance.

3.5.2.2 Hydroxyl-terminated polyethers

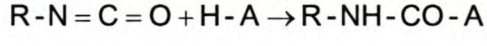
Polyether diols are mainly used for thermoplastic elastomers, fibers and prepolymer-based flexible foams. Polyethers with a functionality of four or greater are usually used in flexible foams, coatings, sealants and elastomers.

3.5.3 Reactions of Isocyanates

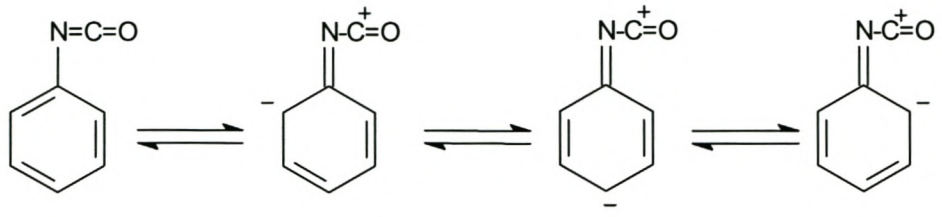
The highly unsaturated isocyanate (-N=C=O) group is very reactive with a wide range of compounds, including itself. It can react with almost any compound containing an active hydrogen. The expected resonance structure is as follows:



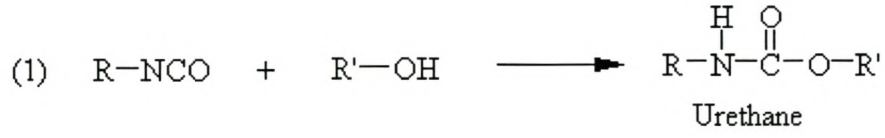
The positive characteristic of the carbon atom makes it susceptible to nucleophilic attack (attacked by electron donor groups), while the negative characteristic of the oxygen or nitrogen atoms makes it susceptible to electrophilic attack (electron accepting groups), e.g. :

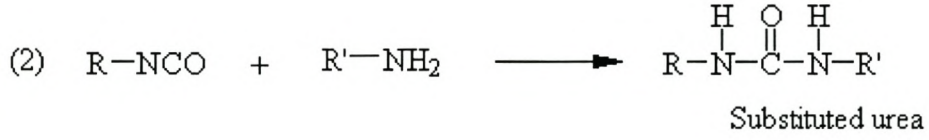


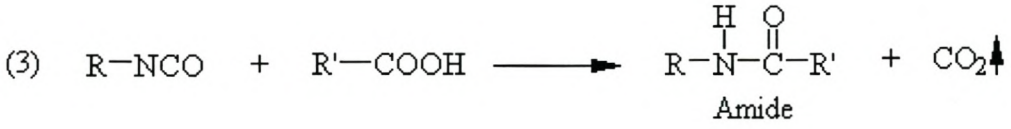
Aromatic isocyanates are more reactive than aliphatic isocyanates. This is due to the delocalization of the negative charge into the aromatic ring, thereby increasing the electrophilic character of the carbonyl ion, as seen in the following scheme.



In addition, electronegative substituents on the aromatic ring increase the reactivity of the NCO-groups, whereas electropositive substituents decrease the reactivity. Steric hinderance on either the isocyanate or the reactive hydrogen compound will retard the reaction. The main reactions of isocyanates are summarised below.







3.5.4 Isocyanate self-reactions

The isocyanate group (-N=C=O) is a highly unsaturated and readily undergoes dimerisation and trimerisation to form uretidiones and isocyanurates respectively.

a. Dimerization

The rate of dimerization of aromatic isocyanates is dependent on the electronic or steric influences of ring substituents. Dimerization is an equilibrium reaction that is greatly retarded by ortho-substituents. Dissociation of these dimers occurs at elevated temperatures and are used for blocked polyurethane coatings[30].

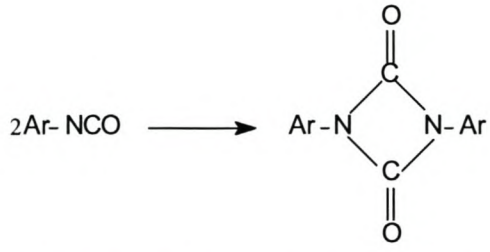


Figure 3.3: Dimerization of an aromatic isocynate

b. Trimerization

Both aliphatic and aromatic isocyanates can form trimers. Trimerization is however not an equilibrium reaction, and can be stable up to 200°C. The rate of trimerization is also greatly reduced by ortho-substituents on aromatic isocyanates.

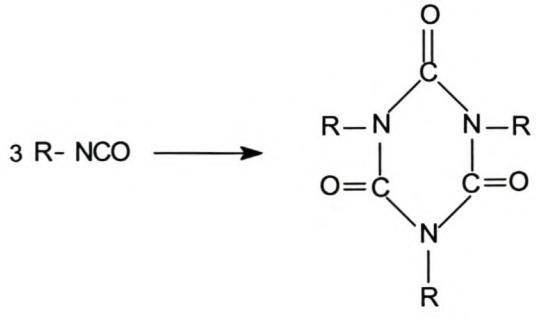


Figure 3.4: Trimerization of both aliphatic and aromatic isocyanates

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4 EXPERIMENTAL

4.1 Introduction

In industry, many different polymers are used to coat paper surfaces in order to obtain a wide variety of properties, including decorative, barrier or functional properties.

Amongst these polymers, polyurethanes (PUs) are the least used for paper coating applications. This is mainly due to their high price, especially that of the isocyanate component. In the past, up-scaling a polyurethane production produced many problems, especially the high reactivity of the isocyanate-group towards impurities such as water, etc. Today, however, the side reactions have been mainly reduced, from being a problem to being under control. Other than the costly price, PUs has almost no other disadvantages.

The advantages of PUs however often outweigh their disadvantages. The main advantage is that the polyurethane can be tailor-made to enhance certain desired properties for a specific application. The desired PU properties required in the paperboard application include: minimum MVTR-values, particle size control, good-excellent film formation properties, wax compatibility, minimum blockage of the coated paperboard to each other, thermal and chemical stability. Other advantages include the characteristic inherent properties of PUs, such as thermal, chemical and abrasion resistance.

Two polyols, one containing 10% phosphorous and the other none, were synthesized for the production of the PU. The first was synthesized to contain two monomers, namely adipic acid and neopentyl glycol (NPG). The idea was to make a linear high molecular mass polyol to ultimately eliminate the use of any crosslinking agents. The PU obtained was immediately tested for the desired properties, after which this information was used to make adjustments for the next batch.

The second polyol synthesized contained four monomers, namely adipic acid, NPG, 1,4-cyclohexane dicarboxylic acid (CHDCA) and 10% 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCA). The purpose of the CHDCA monomer was to increase the hydrophobicity of the polyol, while the PBTCA was added to further enhance the desired properties, especially in terms of barrier properties. The phosphorous-containing monomer can either be incorporated into the soft segment polyol[1,2] or reacted during urethane formation as a chain

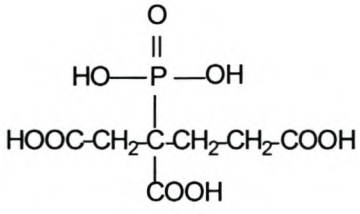
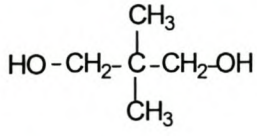
extender[3]. The phosphorous monomer selected contained reactive acid groups, which would thus be incorporated into the macro-diol (polyester polyol).

4.2 Synthesis of Macro-diols

4.2.1 Raw materials

The raw materials for the synthesis of the macro-diol are summarized in Table 4.1 below.

Table 4.1: Macro-diol monomers

Raw materials for macro-diol synthesis	Source
1,4-Cyclohexane dicarboxylic acid (CHDCA) 	Eastman Chemicals
Adipic acid (AA) $HOOC-(CH_2)_4-COOH$	ICI
2-Phosphonobutane-1,2,4- tricarboxylic acid (PBTCA) 	Bayer
Neopentyl glycol (NPG) 	Perstop Polyols

All the monomers were supplied in powder form, except the phosphate-containing monomer, which was supplied in a 50% water solution. This monomer could be added in two states into the reaction mixture. Firstly, the monomer could be concentrated by removing the water

under vacuum at about 100°C, resulting in a solid, hygroscopic, glassy material. Secondly, it could be used as is, since the water can be easily distilled off during the heating process.

4.2.2 Experimental setup

The equipment used to synthesis the polyester macro-diol, is tabulated in Table 4.2 below.

Table 4.2: Equipment used for polyester macro-diol synthesis

Equipment
• Four neck 1 liter glass reactor • Thermocouple • Dean-Starke trap • Mechanical stirrer • N_2-gas • Teflon seals and gaskets • Heating mantle • Temperature control unit • Reflux condenser

4.2.3 Experimental procedure

The solid polyols were first added to the reactor and heated to melt at 100°C (see Appendix 1). This was followed by the addition of the acids under slow agitation. Thereafter the reactor was sealed and purged with nitrogen gas, after which the temperature was increased to 120°C to remove water from the phosphated-monomer. The reaction temperature was then increased to 210-230°C and the reaction mixture stirred at 300-350 rpm. The refluxed water of the polyester condensation reaction, was used to check any glycol loss during the reaction. If glycol was lost, it was replaced. The progress of the reaction was monitored by measuring the acid value obtained by acid-based titrations. As the reaction neared its end-point, the agitation speed was increased to 400-450 rpm to increase the interaction between the reactants.

The reaction took about 12 hours to complete, after which the polyester polyol was cooled to 80°C, dried and degassed under vacuum for 48 hours to remove any traces of moisture, before it was used for the synthesis of the urethane.

4.2.4 Polyol formulation

Formulations of the polyester polyols are shown below in Table 4.3.

Table 4.3: Polyol formulations

Non-phosphate containing polyol		**Phosphate containing polyol**	
Raw material	**Mass %**	**Raw material**	**Mass %**
NPG	45	NPG	48.27
AA	55	AA	22.17
		1,4-CHDCA	19.55
		PBTCA (Solid)	10.00
Polyol properties		**Polyol properties**	
COOH-value	3	COOH-value	6
OH-value	76	OH-value	306

4.3 Calculations

The calculations necessary to monitor the urethane synthesis are explained below.

4.3.1 Acid-value determination

The unreacted carboxylic acid content was visually determined by acid-base titration, using 0.5*N* potassium hydroxide (KOH) and phenolphthalein as indicator.

The procedure[4] involved weighing a small mass of the polyol (about 2 g) into a conical flask and adding 25 ml of a neutral ethylene acetate solution). The mixture was then heated and vigorously stirred until the sample dissolved, after which it was titrated with 0.5*N* KOH using phenolphthalein as an indicator.

The acid number (in mg KOH per g) is calculated by the following formula:

$$\text{Acid number} = (56.1\ VN) / Wt \qquad (1)$$

Where:

V : The volume (in ml) of KOH consumed in the titration.

N : Normality of the KOH titrant.

Wt : Weight (in gram) of the polymer sample.

4.3.2 Hydroxyl-value determination

The hydroxyl value of polymers is generally determined by acetylation of the sample with acetic anhydride in a pyridine solution[4]. The excess anhydride is decomposed by water, and the resulting acetic acid formed in both the hydrolysis and the acetylation process, is titrated with a standard alkali solution and phenolphthalein as indicator.

The acetylating procedure involves weighing a small mass of the polyol (about 2 g) into a conical flask and adding 20 ml of a 1:3 mixture of acetic anhydride and pyridine, in the presence of ethyl acetate for 2 hours at 105°C. This is followed by hydrolysis with hot water.

Thereafter, the flask is connected to a reflux condenser and the contents heated to 105°C for about 1-2 hours to complete dissolution of the material, while occasionally shaking the flask. When the reaction is complete, the content is homogenized with 25 ml of n-butanol. The acid formed is then titrated with 0.5*N* KOH and phenolphthalein as indicator.

The hydroxyl number (in mg KOH per g) is calculated by the following formula:

$$\text{Hydroxyl number} = [56.1 (V_1 - V_2) N] / \text{Wt} + \text{Acid value} \quad (2)$$

Where:

V_1, V_2 : The volume (in ml) of 0. 5*N* KOH used for titration of the sample and the blank respectively.

N : Normality of the KOH titrant.

Wt : Weight (in g) of the polymer sample.

4.3.3 NCO-value determination

Isocyanate groups can be quantitatively determined by either volumetric or spectroscopic techniques. The volumetric determination[3] involves treating the sample with excess amine, followed by a back-titration of the excess amine with hydrochloric acid (HCl) solution. The volumetric procedure involves weighing about 0.5 g of the pre-polymer and 25 ml of toluene into a conical flask, and allowing the mixture to dissolve completely. The solution is then treated with 25 ml of 0.1*N* *n*-butylamine in toluene, and shaken for 15 minutes. This is followed by the addition of 100 ml of isopropyl alcohol and 4-6 drops of 0.1% bromophenol blue indicator solution, followed by the titration with 0.1*N* HCl.

The isocyanate group content (%) is calculated by the following formula:

$$\% [NCO] = [4.202 (V_1 - V_2) N] / Wt \quad (3)$$

Where:

V_1, V_2 : The volume (in ml) of the HCl consumed in the titration of the blank and the sample, respectively.

N : Normality of the KOH titrant.

Wt : Weight (in g) of the polymer sample.

The NCO-group can also be determined by Fourier Transform Infra-Red spectroscopy. This is done by measuring the relationship between the intensity of the band at 2270 cm^{-1} (characteristic of the isocyanate group) and that of the band at 2950 cm^{-1} (CH stretching vibrations, assumed as internal reference). This method is rapid and simple, but a calibration curve has to be prepared. The infrared spectrum obtained is however useful in showing the presence of NCO-groups at 2270 cm^{-1}.

4.4 Synthesis of Polyurethanes

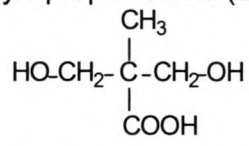
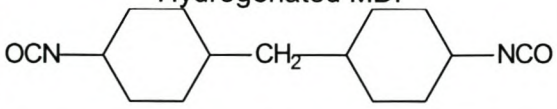
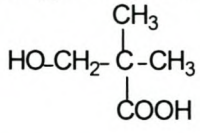
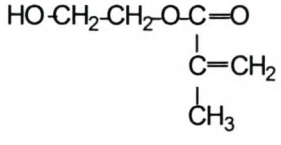
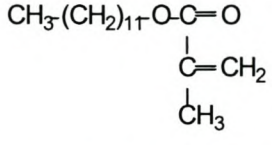
4.4.1 Raw materials

The raw materials used for the synthesis of the PU are summarized in Table 4.4 below. It is very important to eliminate all traces of moisture when making the polyurethane. Thus the reactants were dried as follows prior to use:

- DMPA and HPA were dried overnight at 110°C in a drying oven.
- MEK was dried over a 3Å molecular sieve.
- Polyester polyol was dried and degassed overnight at 80°C in a vacuum oven.

The other reactants were all used as received.

Table 4.4: Raw Materials for PU formulation

Raw materials	Source
Dimethylolproponic acid (DMPA) 	Perstop Polyols
Hydrogenated MDI 	Bayer
3-Hydroxypivalic acid (HPA) 	Perstop Polyols
Hydroxyethylene methacrylate (HEMA) 	BASF
Lauryl methacrylate (LMA) 	Inspec UK Limited
Polyester macro-diol HO------OH	Experimentally synthesized
Triethylamine (TEA) $(CH_3\text{-}CH_2)_3\ N$	BASF

4.4.2 Experimental procedure

The PU was synthesized via the following steps:

- Synthesis of the urethane pre-polymer.
- Neutralization of the pendant carboxylic acid groups.
- Grafting of LMA, n-BMA, MMA and styrene onto the PU.
- Dispersion of PU in water.

4.4.2.1 Synthesis of the urethane

Two types of urethanes, namely a non-phosphated and a phosphated urethane were synthesized by two different methods. This was done by using either the non-phosphated or the phosphated polyester polyol as a soft segment.

4.4.2.1.1 Synthesis of the non-phosphated urethane: Method 1

In this method the DMPA, non-phosphated polyester polyol and H_{12}MDI in MEK-solvent (40% of the total solid content) were reacted at a maximum temperature of 75-85°C while stirring at 160-250 rpm for 2-2.5 hours, to form a segmented urethane polymer with terminal –NCO groups.

Secondly, HPA was added to the reaction mixture at 75-85°C and 250-300 rpm, after which the temperature was decreased to 55-60°C. This step took about 20-30 minutes to complete.

Thirdly, the HEMA and DBTL catalyst were added to the reaction mixture, and the reaction continued at 55-60°C for 2-3 hours to completion.

4.4.2.1.2 Synthesis of the phosphated urethane polymer: Method 2

When synthesizing the urethane polymer using the phosphated polyester macro-diol the addition orders of the monomers were important due to unwanted increase in viscosity. When **method 1** was used for the synthesis of polyurethanes that contain the phosphated polyol, the viscosity of the reaction mixture increased so much, that it appeared as if the whole mixture had crosslinked. This phenomenon could be explained as follows: PBTCA forms a bulky associative side group in the phosphated polyester polyol. This steric and associative effect can cause growing chains to become entangled, forming one huge molecular chain. This increase in chain entanglements restricts molecular mobility, thereby increasing the viscosity to give a "crosslinked" appearance. The addition of more MEK solvent (totaling about 200% of the solid content), however resulted in a considerable drop in the viscosity. The resulting dispersions gave a highly viscous polyurethane emulsion at even 26.5% solid content, with a wide particle size distribution. Therefore a different order of addition was used to control the viscosity and the particle size.

This method (see Appendix 2 for detail) involved synthesizing part of the hard-segment by reacting the DMPA and H_{12}MDI in MEK (40-50% of the total MEK-solvent amount) at 75-85°C and 150-200 rpm for a total of 1-1.5 hours as a first step.

Secondly, the phosphated polyol was pre-mixed with MEK-solvent (50-60% of the total MEK-solvent amount), and then added to the reaction mixture. The reaction was continued for about 2 hours at 75-85°C and 200-250 rpm.

HPA and HEMA were then added in the same procedure as **Method 1**.

4.4.2.2 Neutralization of the pendant carboxylic acid groups

The calculated amount of the neutralizing agent (triethylamine) was added dropwise to the pre-polymer solution at 50°C for about 30-60 minutes to obtain the anionomer. The amount of the neutralizing agent needed could be calculated using the following equation:

$$\text{Mass of neutralizing agent} = \frac{m.(A.V).(E.A)}{5.61 \times 1000} \qquad (4)$$

Where:

- m: The mass of the solid polymer
- A.V: Acid value of the solid polymer
- E.A: Equivalent weight of the neutralizing agent

4.4.2.3 Grafting and dispersion into water

The grafting agents used included: lauryl methacrylate (LMA), n-butyl methacrylate (BMA), methyl methacrylate (MMA) and styrene. The non-phosphated polyurethane only contained the LMA grafting agent, while the phosphated polyurethane contained each of the four grafting agents. The grafting agent and the potassium persulphate initiator (0.02% of the solid content) were added to the anionomer solution at 45-55°C, and reacted over a period of 1.5-2 hours. Water was added afterwards to convert into dispersion and adjust the final solids content to 26.5%. The emulsion was formed and allowed to homogenize at an increased stirrer speed of 300-350 rpm for 30-45 minutes at 40°C, and the MEK was removed by rotary evaporator.

An attempt to first form the dispersion and then grafting in the aqueous phase was unsuccessful, as droplets of monomers were still floating in the reaction mixture after 4 hours at a temperature of 60°C.

4.4.3 Polyurethane reaction scheme

Figure 4.1 below contains the PU reaction scheme.

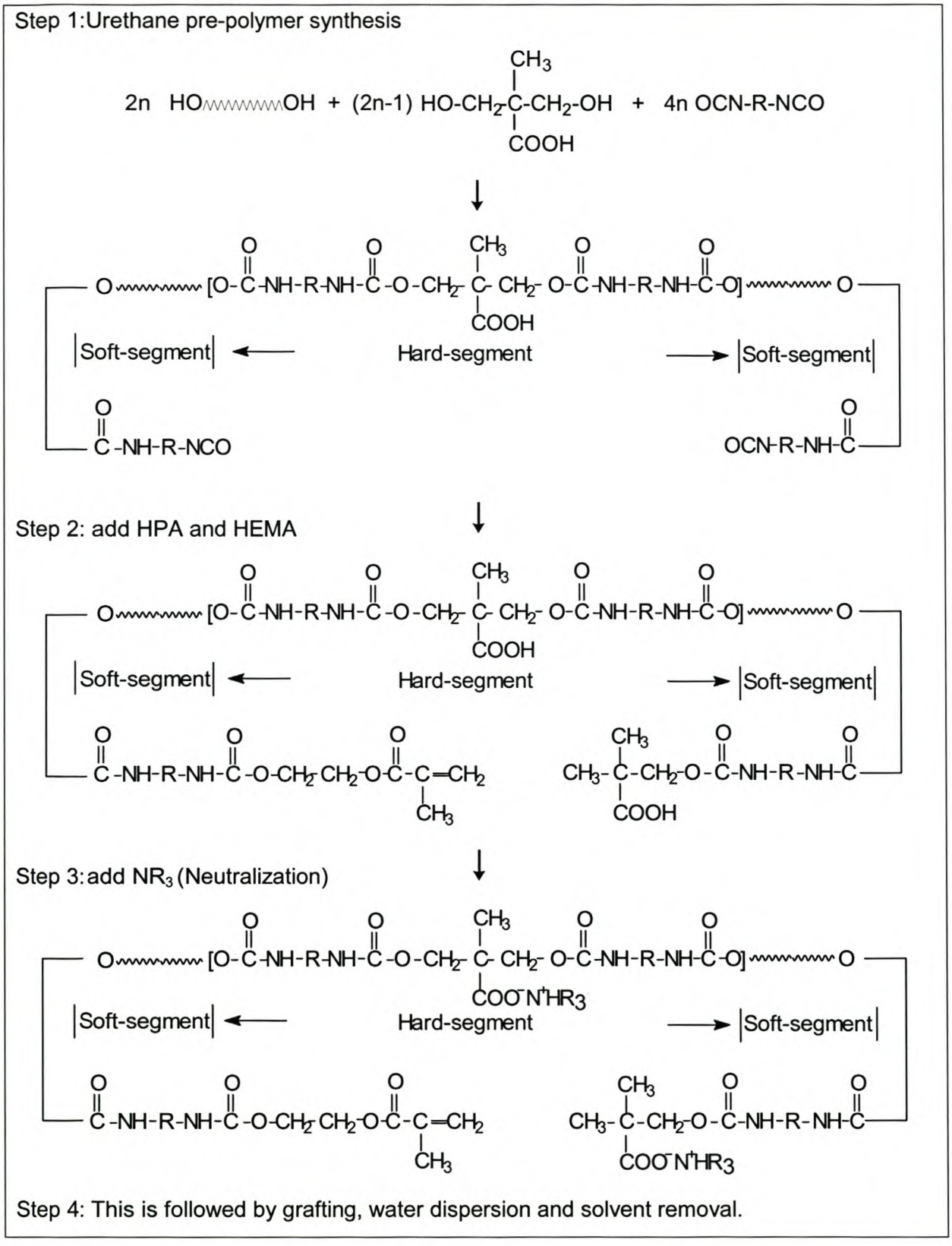


Figure 4.1: PU reaction scheme

4.4.4 Polyurethane formulation

In summary, the formulations containing both the phosphated and non-phosphated PU are shown in Table 4.5 and 4.6, respectively.

Table 4.5: Non-phosphate containing polyurethane

	PU-1	**PU-2**	**PU-3**	**PU-4**	**PU-5**	**PU-6**
Raw materials	Mass (g)	Mass (g)	Mass (g)	Mass (g)	Mass (g)	Mass (g)
Polyol	187.00	175.49	174.91	175.19	185.00	164.00
DMPA	18.51	14.22	13.45	12.00	9.58	7.90
H_{12}MDI	80.62	63.57	52.23	59.16	70.00	51.15
HPA	10.01	12.07	5.06	12.07	9.58	8.03
HEMA	16.20	16.04	13.05	16.04	15.50	13.00
MEK-solvent	125.00	113.00	105.00	110.00	116.00	98.00
Total (excluding the solvent)	312.34	281.39	258.7	274.46	289.66	244.08
DBTL	0.0041	0.0040	0.0033	0.0040	0.0039	0.0033
Et_3N	20.28	20.20	13.00	17.50	20.28	11.57
[NCO]/[OH]	0.84	0.80	0.77	0.79	0.84	0.78
mol.HPA/mol. (HPA+HEMA)	41%	45%	30%	45%	41%	40%
% Soft-Segment	59.9%	62.4%	67.6%	63.8%	63.1%	67.2%
gram COOH per gram Polymer	7.9%	7.5%	5.0%	6.9%	5.5%	4.6%
Chain extension via grafting (0-20% of the PUs total solid content)						
Grafting agent	LMA	LMA	LMA	LMA	LMA	LMA
Emulsification Water was added to obtain an PU-emulsion of 26.5% Solids Content						

Table 4.6: Phosphate containing polyurethane

	PU-7	PU-8	PU-9	PU-10
Raw materials	Mass (g)	Mass (g)	Mass (g)	Mass (g)
Polyol	120.03	120.10	120.05	120.09
DMPA	6.60	6.62	6.61	6.60
$H_{12}MDI$	52.60	52.56	52.55	52.62
HPA	2.93	2.93	2.93	2.93
HEMA	6.06	6.06	6.06	6.06
MEK-solvent	112.00	112.10	112.14	112.06
Total (excluding solvent)	188.22	188.27	188.20	188.30
DBTL	0.0015	0.0015	0.0015	0.0015
Et_3N	11.06	11.08	11.04	11.05
[NCO]/[OH]	0.77	0.77	0.77	0.77
Mol.HPA/mol. (HPA+HEMA)	36%	36%	36%	36%
% Soft-Segment	63.8%	63.8%	63.8%	63.8%
gram COOH per gram Polymer	2.6%	2.6%	2.6%	2.6%
Chain extension via grafting (0-16% of the PUs total solid content)				
Grafting agent	LMA	n-BMA	MMA	Styrene
Emulsification: Water was added to obtain an PU-emulsion of 26.5% -solids content				

4.5 Polyurethane-Wax Composites

The determination of the optimum percentage wax in the PU/wax compositions for paper coating is explained in Appendices 3,4 and 5. Appendix 3 shows the screening of 23 of Schumann Sasol's waxes with the synthesized PU to obtain the lowest MVTR values, of which wax A15/31 and wax C78 were the most promising.

Appendix 4 shows the determination of the optimum percentage wax to the PU/wax composition that would give the lowest MVTR-value. It shows that an optimum of 15% wax should be included in the PU/wax composition.

Appendix 5 lists the characteristic properties of wax A15/31 and wax C78.

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5 ANALYTICAL TECHNIQUES

Several analytical techniques were used during the synthesis of the polymer, as well as to characterize the final product. The following analytical techniques were used:

- Fourier Transform Infrared Spectroscopy (FTIR)
- Dynamic Mechanical Analysis (DMA)
- Particle size analysis
- Scanning Electron Microscopy (SEM)
- Thermogravimetric Analysis (TGA)
- Differential Scanning Calorimetry (DSC)
- Moisture Vapour Transmission Rate (MVTR)
- Dynamic Contact Angle Analysis (DCA)
- Blocking test

5.1 Fourier Transform Infrared Spectroscopy

FTIR-analysis is used to follow and characterize the emerging and disappearing functional groups during PU synthesis[1-3]. During the synthesis of the PU, FTIR samples were prepared by extracting some polymer from the reactor vessel and dissolving it in MEK solvent. The sample was then run against a MEK background between sodium chloride (NaCl) discs on the Perkin Elmer 1650 instrument (at 4 scans). This was done to monitor the NCO-content during the polyurethane synthesis. All other infrared analyses were performed on a Perkin Elmer Paragon 1000 FTIR instrument at 128 scans, using a photo-acoustic cell, eliminating sample preparation.

5.2 Dynamic Mechanical Analysis

Dynamic mechanical analysis[4-7] measures the mechanical properties of a material, such as the modulus (stiffness) and damping (energy dissipation) as a function of temperature and frequency under periodic (oscillatory) stress. Material types that can be analyzed include coatings, adhesives, elastomers, composites, viscous thermoset liquids, ceramics and metals. The properties that can be obtained by means of the DMA technique, is listed in Table 5.1, of which the glass transition temperature (T_g) was especially important:

Table 5.1: Properties obtained from analysis by DMA technique

Modulus	Degree of cure
Glass transition temperature (T_g)	Rate of cure
Gelation	Sound absorption correlations
Damping characteristics	Impact resistance correlations
Viscosity	Polymer morphology

The DMA-samples were prepared by first drying the PU-emulsions in Teflon holders for ±6 hours at 90°C. The dried samples were pressed into thin films (100-250μm) under 10-ton pressure at temperatures between 30-190°C. The pressed films were analyzed on a Perkin Elmer DMA 7e instrument, coupled to a thermal analyzer controller model TCA 7/DX, using a 1mm probe and N_2 carrier gas set at a pressure just below 200 kPa.

5.3 Particle size analysis

Particle size analysis of the polyurethane emulsions was done on a Zetasizer 1000HSa instrument from Malvern Instruments. The instrument was first calibrated with a nano-standard with a particle size of 220 nm, before a urethane sample was run. The desired particle sizes of the ungrafted PU dispersions should be between 100 to 150 nm.

5.4 Scanning Electron Microscopy

Scanning electron microscopy[8-10] (SEM) was used to evaluate the surface characteristics of the PU samples, which especially included pinholes in the PU coated paperboard. The SEM instrument model ABT-60 from Topcon, using *Analysis Image Capturing* software from *Soft Imaging System*, was used. The images were obtained at 7kV at a working distance of 10 mm, using secondary electron imaging.

Samples were prepared by cutting the dry coated paperboard into small blocks of about 1 cm^2. Samples were coated with a thin micro-layer (± 1-2 molecular layer) of 24 carat gold. This was done to increase the sample's electron transferring abilities, so as to obtain a clearer image.

5.5 Thermogravimetric Analysis

Thermogravimetric analysis[5,6,11,12] (TGA) measures the percentage weight change of a material as a function of temperature or time in a controlled atmospheric environment. The measurements are primarily used in determining the composition of materials and to predict their thermal stability at temperatures up to 1000°C. Other useful information obtained from TGA measurements includes oxidative stability, lifetime estimations, decomposition kinetics, different atmospheric effects, and the moisture and volatile content of materials.

The PU samples were analyzed in terms of their thermal stabilities on a TGA 7 instrument from Perkin Elmer.

5.6 Differential Scanning Calorimetry

Differential scanning calorimetry[5,6,13,14] measures heat flow associated with transitions in materials as a function of time and temperature. It is primarily used in the characterization of polymers and organic materials. The properties that can be obtained by means of the DSC technique are listed in Table 5.2 below:

Table 5.2: Properties obtained from analysis by DSC technique

Glass transition temperatures	Reaction kinetics
Melting temperatures	Thermal stability
Crystallisation time and temperature	Oxidative stability
Specific heat capacity	Curing rates
Heat of reaction and fusion	Degree of cure
Compatibility of polymer blends	Purity

The samples were analyzed on a Pyris 1 instrument from Perkin Elmer.

5.7 Moisture vapor transmission rate determination

The moisture vapor transmission rate (MVTR) of coated paper was determined using a Heraeus Votsch humidity cabinet, Type VTRK 300. The method employed was based on the method of Mondi Cartonboard (see Appendix 6). The experiments were performed at tropical conditions, i.e. at 38°C and 90% relative humidity (RH). The objective was to synthesize a PU coating having an MVTR-value below 200 g/m^2/24h at tropical conditions.

Sample preparation:

Emulsion coatings, consisting of either a pure PU or a composite PU/wax mixture, were applied to Mondi cartonboard by means of a threaded coating bar, equipped with end-fittings to prevent it from rolling during the coating process. These coating bars were used in conjunction with a coating machine (Maans Fourie Machines) to ensure reproducibility during the coating process. The coating was applied to the paperboard at an average coating speed of 0.067m/s, after which it was cured in an oven at approximately 110°C for a period of 10 minutes. The amount of coating applied to the paperboard was calculated according to the method described in Appendix 6. These coated circles were consequently used for the determination of the MVTRs as described in Appendix 4.

5.8 Blocking test

The blocking test was done to determine whether a pallet of coated paperboard sheets would stick to each other or not as a result of the applied coating. The test involved putting a 28 kg weight that applied ±0.5 bar pressure on a surface of the stacked coated paperboards for a period of 24 hours at ±22°C. After 24 hours, the samples were removed from the device and carefully pulled apart, notifying the amount of sticking (blocking) that occurred (see appendix 7 for the blocking test method and the different levels of blocking).

5.9 References

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6 RESULTS

The results of the analytical techniques used for the characterization of the PU samples as discussed in Chapter 5, are explained in this chapter.

6.1 Fourier Transform Infrared Spectroscopy

FTIR analysis was employed firstly to monitor the consumption of raw materials during the synthesis of the PU, and secondly for the characterization of the pre-polymer and the PU itself.

6.1.1 NCO content

The presence of the free –NCO during the synthesis of the urethane prepolymer is shown in Figure 6.1a. It clearly showed the presence of the isocyanate in the reaction mixture, which is represented by the NCO-peak at 2260 cm^{-1}.

Figure 6.1b the absence of the characteristic-NCO peak at 2260 cm^{-1} indicates that all the isocyanate groups were reacted with HPA and HEMA during the chain extension step. This is very important, as NCO-groups should be avoided when water is added to form the urethane dispersion. If there are NCO-groups present during the addition of water, this will result in the formation of a crosslinked structure.

6.1.2 Characterization of the polyurethane

FTIR analysis was done on the dried films of the PU emulsions synthesized. Figures 6.2 to 6.8 contain the FTIR spectra of the polyols and PUs synthesized. The band at 1732 cm^{-1} in all the IR-spectra, represents the carbonyl group (C=O). It is clearly the dominant peak in the polyol IR-spectrum (Figure 6.2), but it decreases in size in the PU IR-spectrum (Figure 6.3). This is due to no additional ester groups being formed during urethane formation[1].

The absorption bands between 2800-3000 cm^{-1} are due to C-H stretching of the CH_2 and CH_3 groups[2]. This peak is not the dominant peak in the polyol IR-spectrum (Figure 6.2), but it increases in size to become the dominant peak in the PU IR-spectrum (Figure 6.3), due to the addition of C-H containing monomers, i.e. HEMA, DMPA, HPA and H_{12}MDI.

The absorption bands in the polyol FTIR-spectrum (Figure 6.2) between 3200-3350 cm^{-1}, represent the OH-groups of the polymer. These OH-peaks disappear in the PU FTIR-

spectrum (Figure 6.3) and are dominated by the NH-stretching band at about 3340 cm^{-1} of the urethane group. The peak at 1520-1530 cm^{-1} in the PU FTIR-spectrum (Figure 6.3) represent the NH deformation vibration[2].

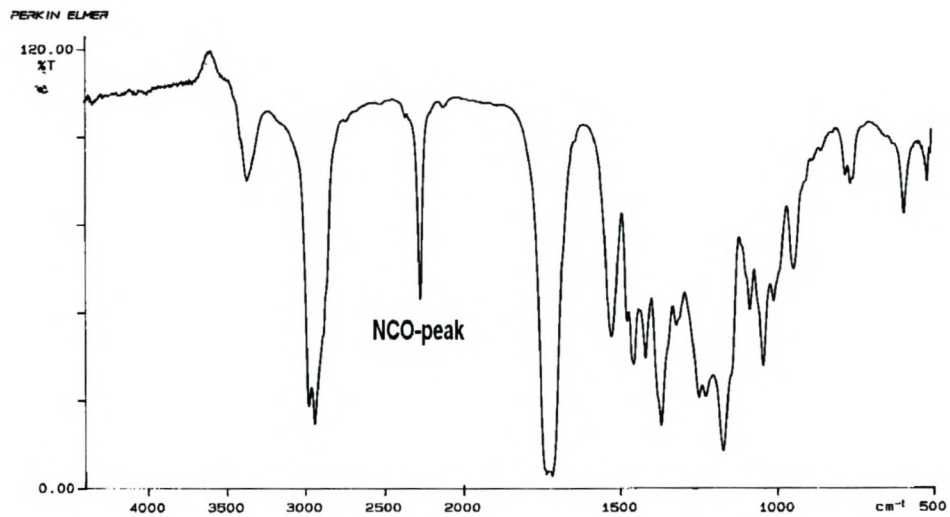
The band at 1378 cm^{-1} in the polyol FTIR-spectra (Figure 6.2), represents the C-CH_3 (symmetrical) deformation, while the bands between 1140-1246 cm^{-1} represent the C-O stretching deformation.

The phosphoryl linkage (P=O) in organic compounds has a broad absorption range at 1080-1450 cm^{-1}[1,3,5]. The effect of strong H-bonding results in large frequency shifts to a lower absorption range. H-bonding resulting from P-OH groups is subjected to shifts of 50-80 cm^{-1}. Phosphated compounds containing (HO)-P=O groups have an even stronger H-bonding, which results in larger frequency shifts and increases in intensity. This increase in intensity can be clearly seen by comparing the IR-spectra of the two polyols (Figure 6.2) in the frequency range of 1004-1036 cm^{-1}.

Thomas and Chittenden determined an overall phosphoryl absorption range of 1087-1261 cm^{-1}, based on the evaluation of 160 organic compounds containing (HO)-P=O or $(HO)_2$-P=O groups[4]. Thus the absorption peaks in the polyol IR-spectrum (Figure 6.2b) at 1004 and 1036 cm^{-1} can be assigned to P=O stretching vibrations[3,5].

Figure 6.4 represent the IR-spectra of 4 and 8% grafting of LMA onto the non-phosphated polyurethane polymer. The rest of the IR-spectra (Figures 6.5 to 6.8) represent the grafting of MMA, n-BMA, LMA and styrene onto the phosphated polyurethane. From these spectra, it can be seen that the FTIR technique is not sensitive enough to distinguish between the different grafting agents used. This can be attributed firstly to the fact that the repeating units of the grafting agents are very similar to that of the PU, and secondly to the fact that the grafting agents are only present in low concentrations.

(a) The presence of NCO-groups during PU synthesis



(b) The absence of NCO-groups during PU synthesis

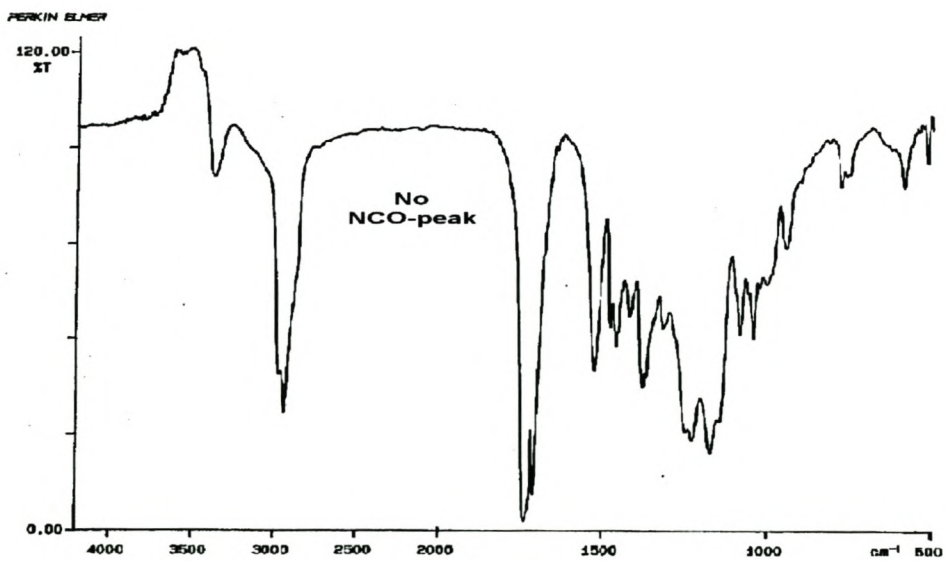


Figure 6.1: Monitoring the NCO-content during the PU synthesis by FTIR, at 4 scans, 4.0cm^{-1}

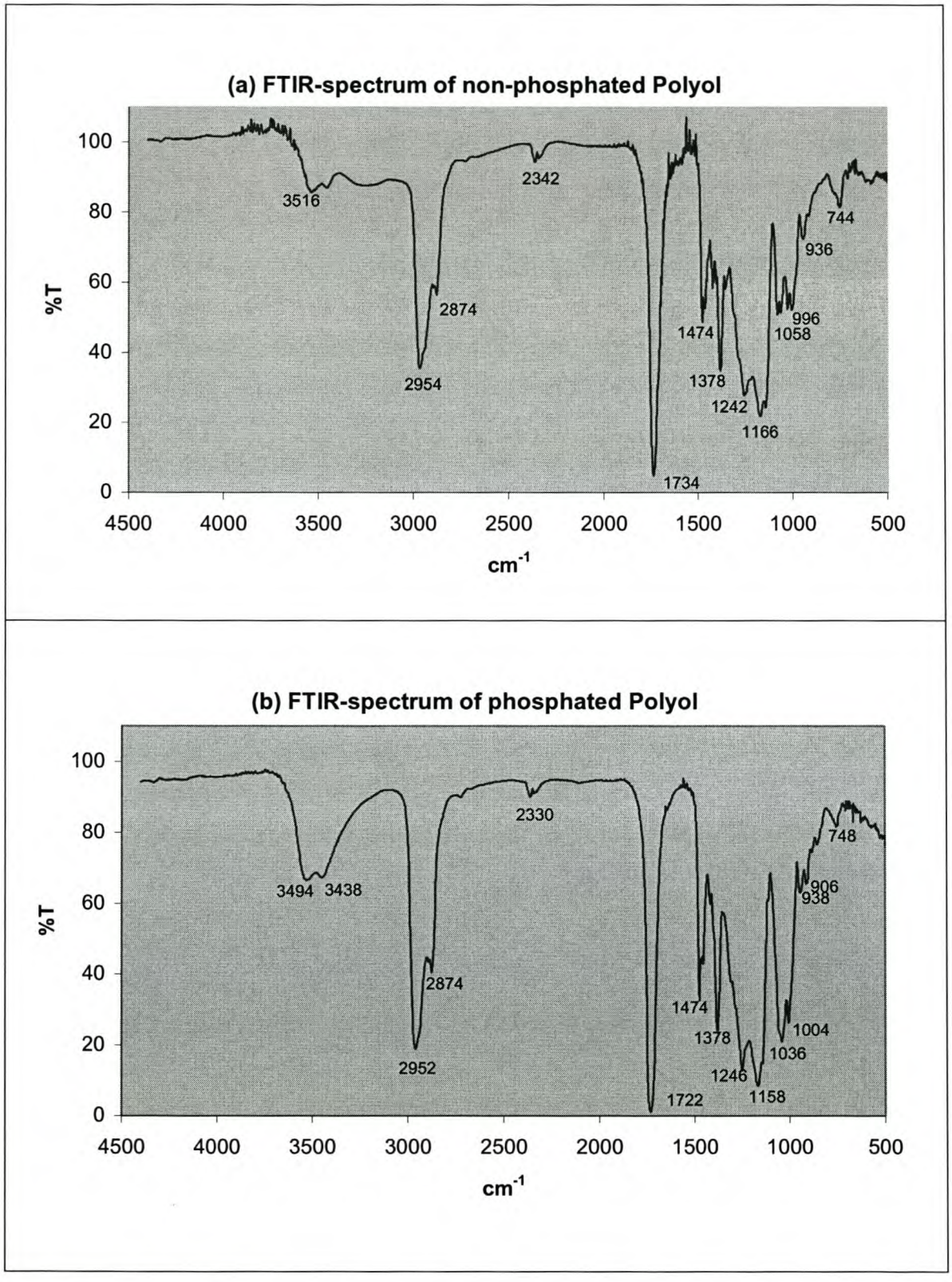


Figure 6.2: FTIR-spectra of the phosphated and non-phosphated Polyol

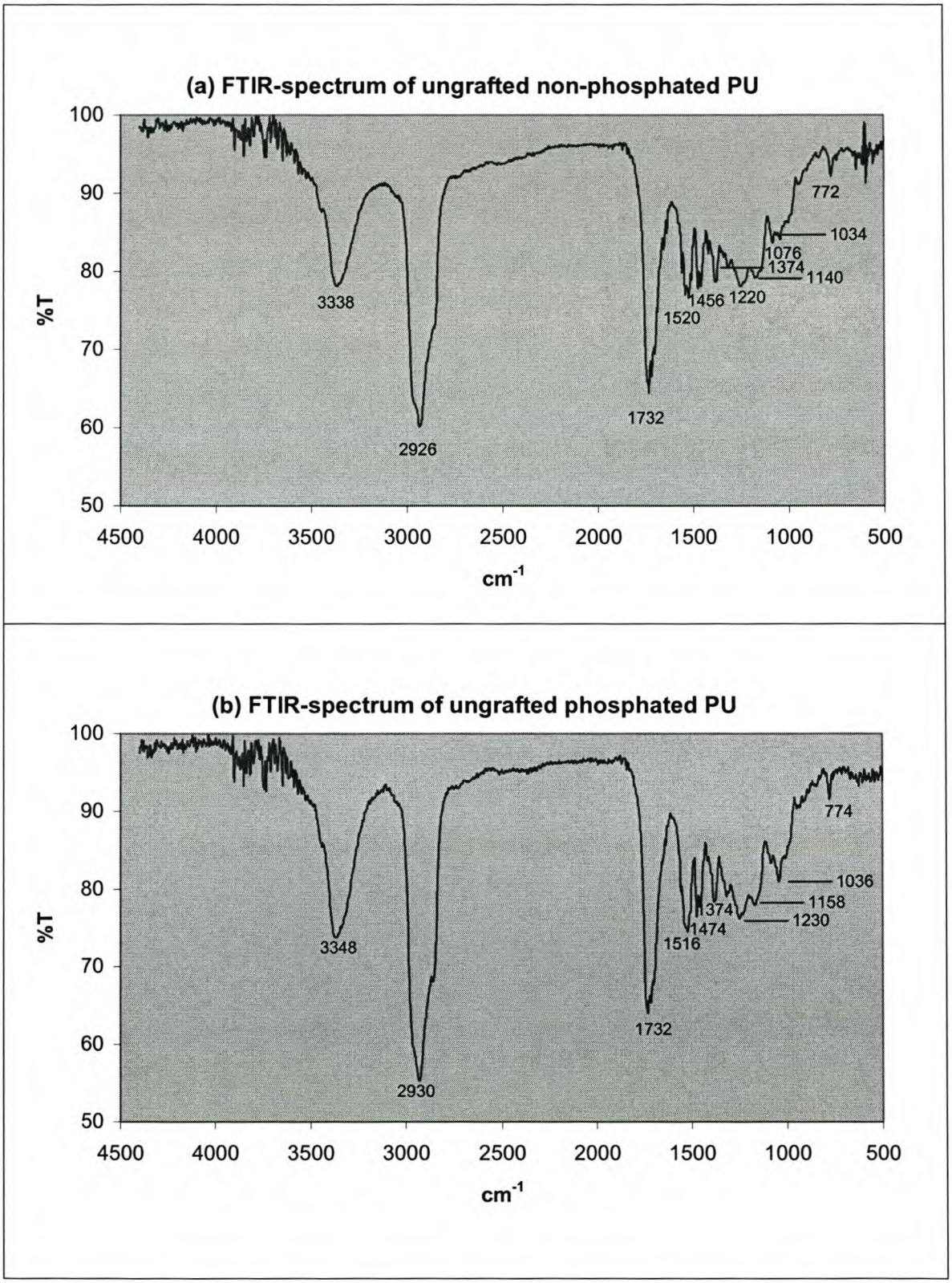


Figure 6.3: FTIR spectra showing the effect of phosphate on the ungrafted PU

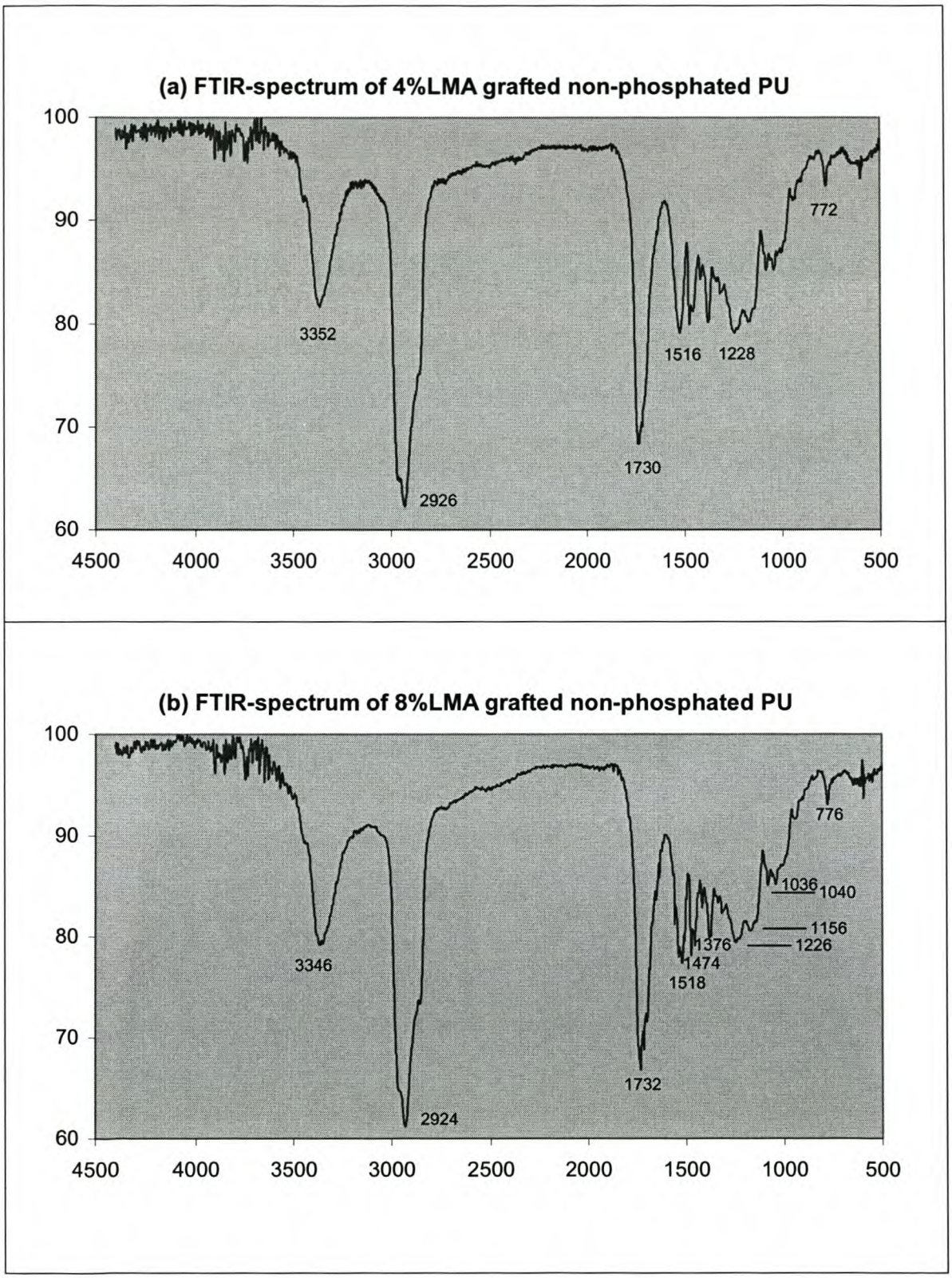


Figure 6.4: FTIR spectra showing the effect of % LMA on the non-phosphated PU

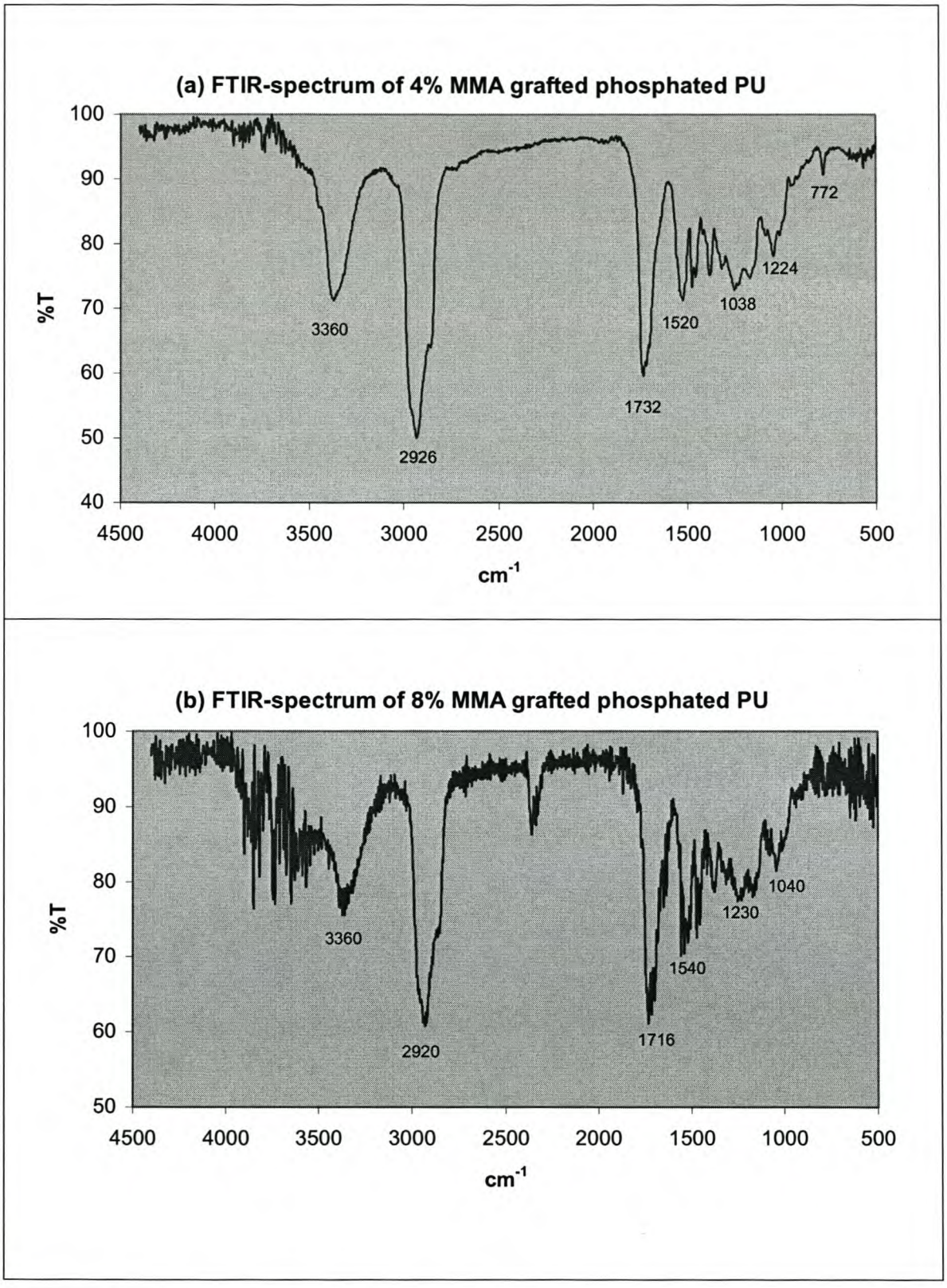


Figure 6.5: FTIR spectra showing the effect of % MMA on the phosphated PU

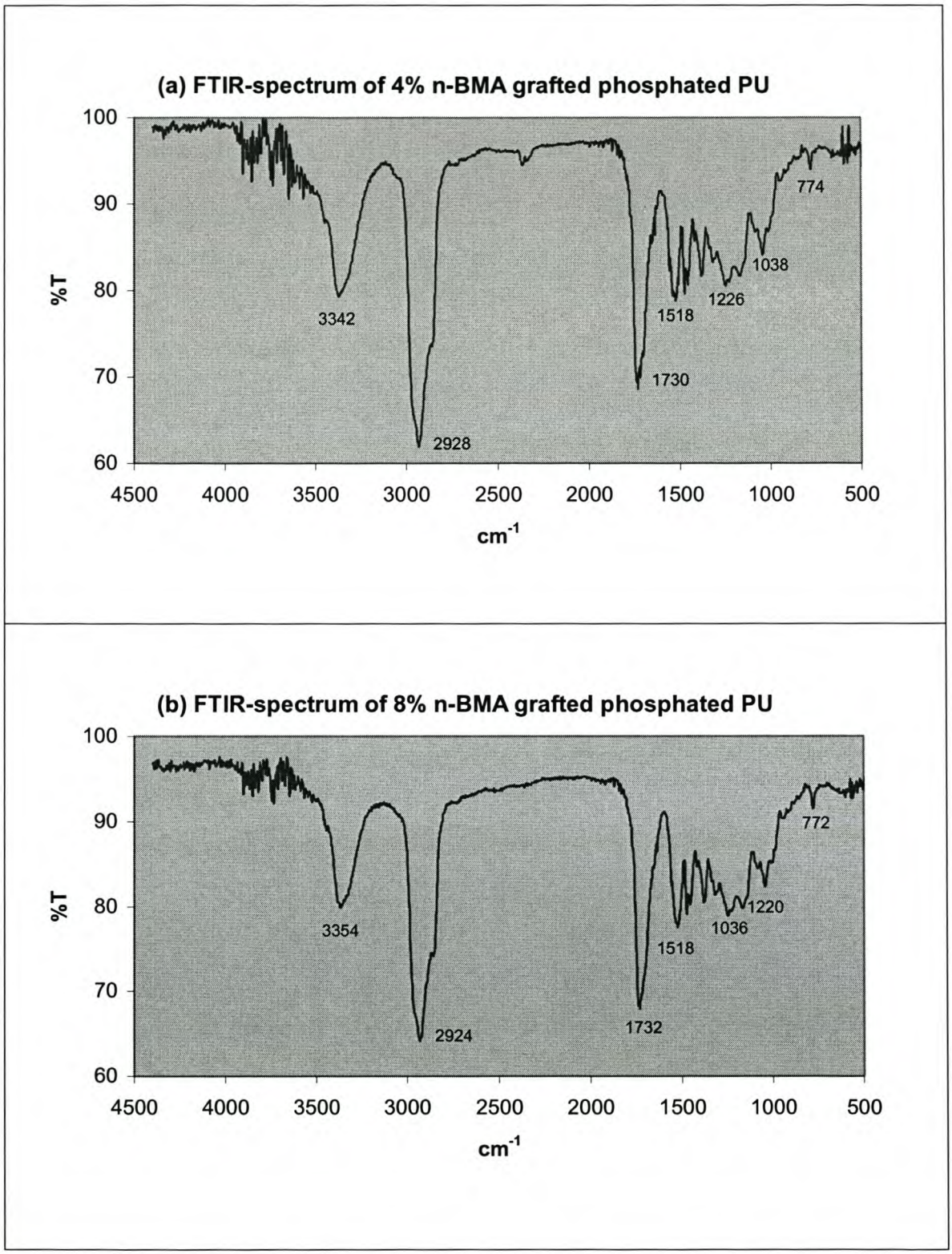


Figure 6.6: FTIR spectra showing the effect of % n-BMA on the phosphated PU

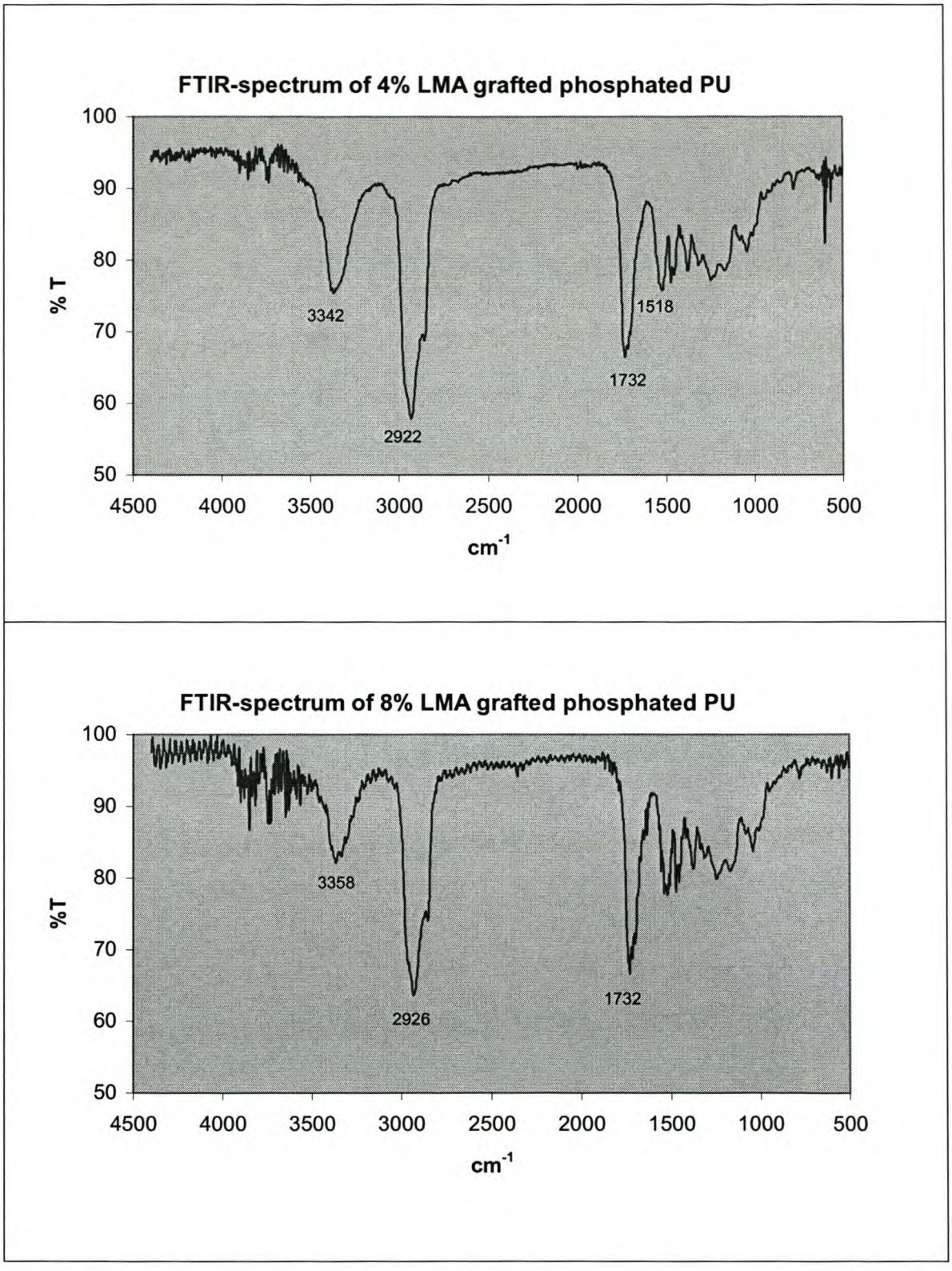


Figure 6.7: FTIR spectra showing the effect of % LMA on the phosphated PU

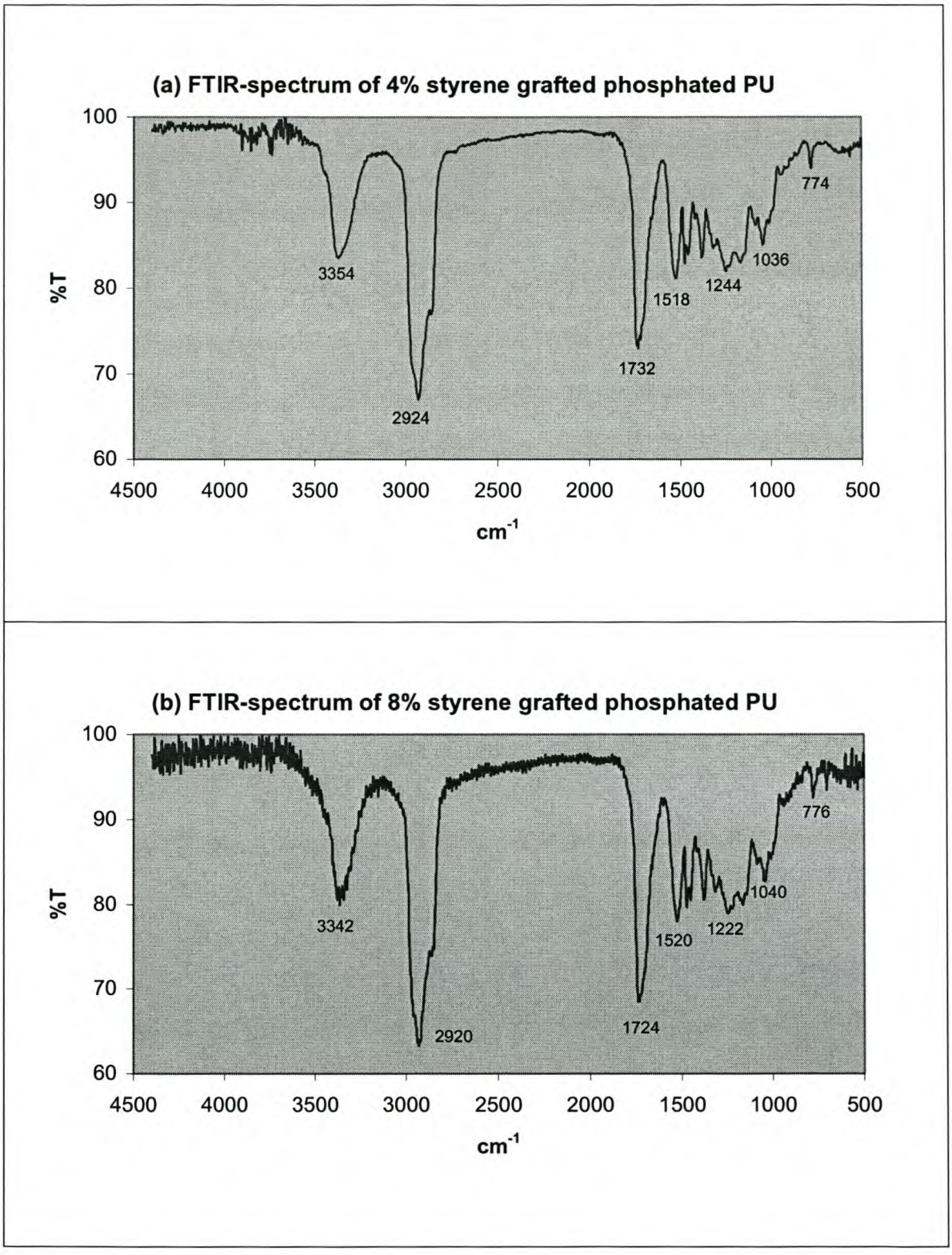


Figure 6.8: FTIR spectra showing the effect of % Styrene on the phosphated PU

6.2 Dynamic Mechanical Analysis

Dynamic mechanical analysis gives an insight into the microstructure of the PU[6-11].

6.2.1 Effect of phosphated polyol on the polyurethane

The non-phosphated PU-films have a lower T_g than the phosphated PU-films (Figures 6.9 and 6.10). Yet when looking at the shape of the T_g -peaks, it seems that the soft and hard segments in the non-phosphated PU-films are reasonably compatible, seen as a second hump in the tan δ curve (Figure 6.9), while the soft and hard segments in the phosphate PU-films show no signs of incompatibility.

6.2.2 Effect of grafting agents on the polyurethane

The effect of the grafting agents is clearly visible in the case of the phosphated PU samples (Figures 6.10(a,c,d)). At 4% grafting, the T_g is reduced, but at a minimum of 8% grafting, the T_g seems to increase above the T_g at 0% grafting. It is possible that at 4% grafting the % grafting agent is too low to impart any additional crystallinity into the PU-structure. It was found, however, that it had the opposite effect; there was a decrease in the T_g. At a minimum of 8% grafting, however, the % grafting agent is high enough to impart additional crystallinity into the PU structure, thereby increasing the T_g.

6.2.3 Effect of semi-crystalline waxes on the polyurethane

The addition of the semi-crystalline waxes to the urethane matrix has no clear effect on the compatibility of the soft and hard segments of the phosphated PU (Figure 6.11(c) and (d)). The T_g decreases systematically as the % wax is increased from 15-30%. However, in the case of the non-phosphated polyurethanes, the addition of waxes does seem to increase the incompatibility between the hard-and-soft segments (Figure 6.11(a) and (b)). At 15% wax addition, the T_g is decreased, but at 30% wax addition the T_g increases. This could be due to the wax co-crystallizing with the soft segment of the PU at 30% wax addition, thereby increasing the T_g to a higher temperature. Furthermore, during the drying of the non-phosphated PU samples containing 15 and 30% wax, it was noted that the brittleness of the dried samples decreased from 0 to 30% wax.

6.2.4 Semi-crystalline waxes

DMA-analysis of the individual waxes is contained in Figure 6.12(a-c). Figure 6.12(a) shows that Wax A15/31 consists of a mixture of two waxes; one has a T_g onset in the range of –45°C, and the other an onset at about +15°C.

Wax C78 was similar to Wax A15/31, in that it has two separate T_g's (Figure 6.12(b)). It should however be mentioned that the sample preparation for wax C78 differed from that of wax A15/31. When wax C78 was being dried for 6 hours at 90°C, a hard dry crust formed on the surface, while the bottom part remained a liquid, even after it was cooled to room temperature. The temperature was then increased to 130°C for another 1-2 hours to dry the sample. When analysed, the dried wax seemed to separate into two fractions, one being a softer white fraction and the other a harder yellowish fraction. From these two fractions came the two T_g peaks in Figure 6.12(a). The two fractions were also pressed together under 10 tons at about 60°C, resulting in the third T_g peak seen in Figure 6.12(c). This shows that the two separate T_g peaks joined, to form one T_g peak.

6.2.5 Conclusions

The inclusion of phosphate in the PU-formulation has a clear effect on the mechanical properties of the PU-films. The effect is summarized in Table 6.1 below:

Table 6.1: Effect of phosphate in PU formulation on mechanical properties of PU

Non-phosphated PU films	Phosphated PU films
Lower T_g.	Higher T_g.
Reasonable compatibility between hard- and soft segments of the PU, with or without wax addition.	No incompatibility between hard- and soft segments of the PU, with or without wax addition.
15% wax decreases the T_g, after which 30% wax increase the T_g.	The T_g decreases proportionally with increased wax addition from 0 to 30%.

The higher T_g of the phosphated PU-films can be expected due to the increase in hydrogen bonding and chain entanglements from the bulky phosphate group, resulting in a more rigid structure, thereby increasing the T_g.

6.3 Particle Size Analysis

Each of the PU-emulsion samples underwent five runs on the Particle Analyzer, of which the average particle size (ZAve) of each run is tabulated above their corresponding graph in Figures 6.13-6.18.

Results of the particle size analysis of the ungrafted phosphated PU, synthesized via synthesis method 1 (See section 4.4.2.1.2), showed it to be very broad, as seen from Figure 6.13. This particle size distribution is unfavorable, due to its high solvent uptake (up to 250% of the solid content) during the polyurethane synthesis. The idea was to minimize the amount of solvent used in the PU formulation[12-13].

In contrast, Figure 6.14 shows a much narrower, and therefore more favorable particle size distribution for the ungrafted polyurethane synthesized via synthesis method 2 (See section 4.4.2.1.2). Its solvent usage is only 40-60% of the urethane's solid content, and is therefore much more favorable than the solvent consumption of method 1.

Figures 6.15 to 6.18 show the particle size distribution of the LMA-grafted PU, also synthesized via synthesis method 2. The grafting seemed to be successful, especially in terms of the increasing particle size with increasing amount of grafting agent, and also the fact that homo-polymerization of the grafting agent is minimal to none.

Run	Angle	KCps.	ZAve	Poly	Fit
1	90	158.7	330.8	0.397	0.000230
2	90	159.9	349.3	0.689	0.000207
3	90	159.5	348.8	0.847	0.000271
4	90	161.5	359.5	0.891	0.000251
5	90	159.4	325.2	1	0.000247
Average		159.8	342.7	0.765	
+/-		1	14.2	0.234	

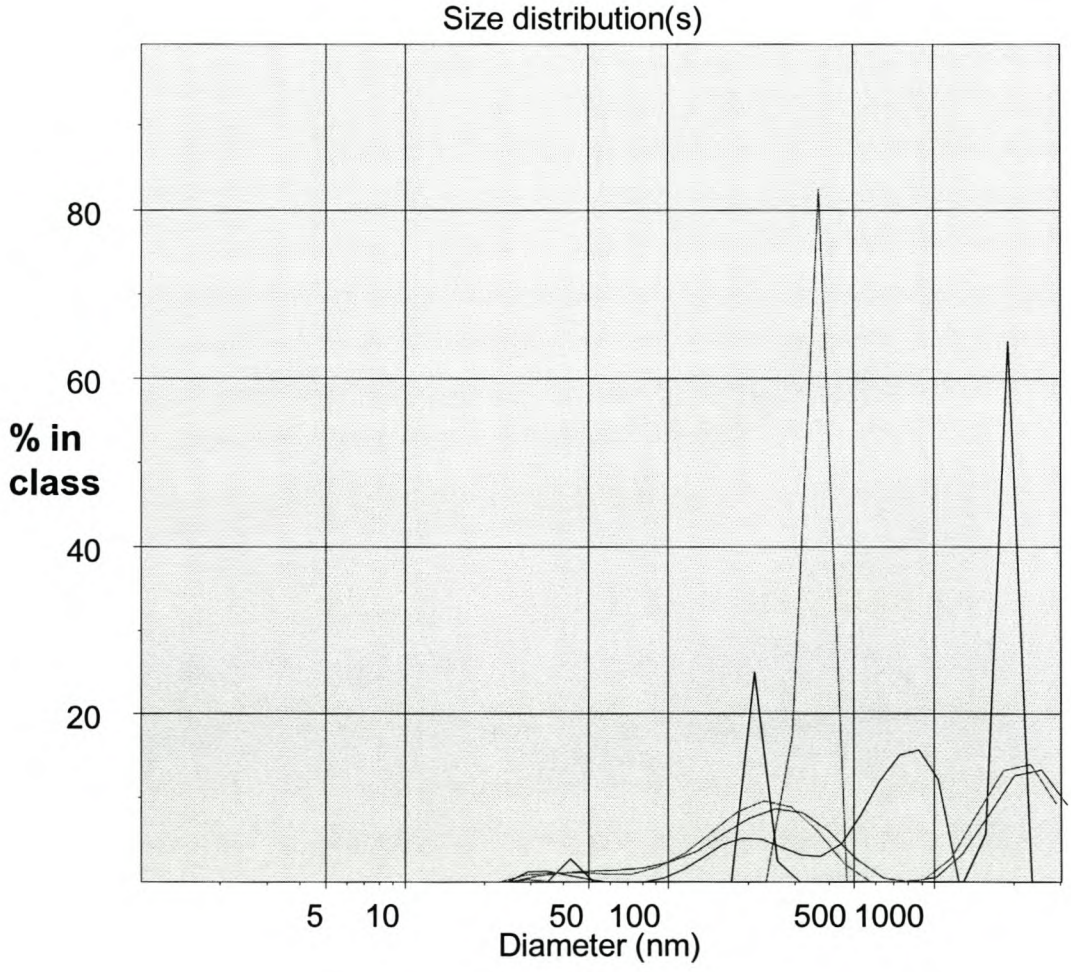


Figure 6.13: Particle size distribution of ungrafted phosphated PU prepared via urethane synthesis method 1

Run	Angle	KCps.	ZAve	Poly	Fit
1	90	116.4	110.2	0.168	0.000497
2	90	117.0	108.2	0.212	0.000440
3	90	117.4	108.5	0.208	0.000241
4	90	117.1	107.7	0.177	0.000253
5	90	117.2	108.0	0.200	0.000324
Average		117.02	108.52	0.193	
+/-		0.4	1.0	0.020	

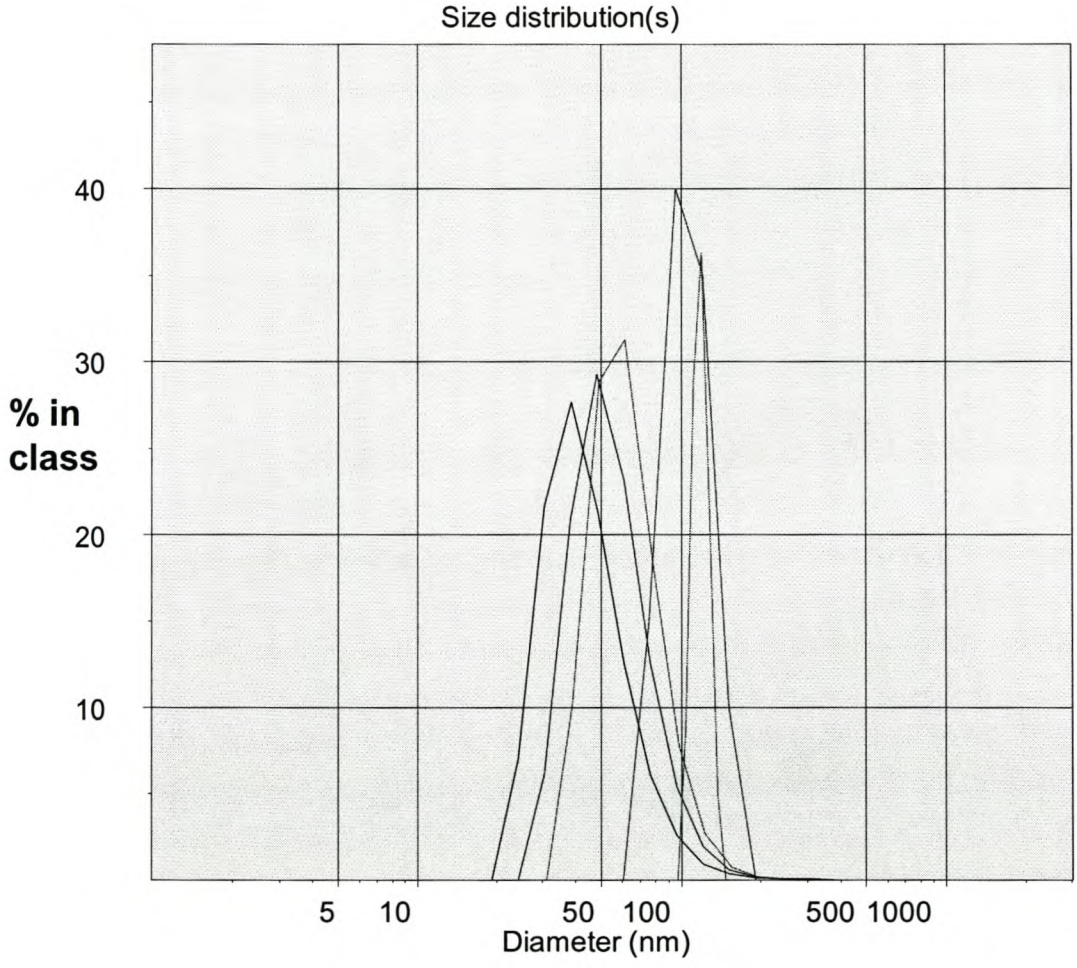


Figure 6.14: Particle size distribution of ungrafted phosphated PU prepared via urethane synthesis method 2

Run	Angle	KCps.	ZAve	Poly	Fit
1	90	142.8	138.6	0.141	0.000372
2	90	142.7	135.7	0.183	0.000359
3	90	142.7	136.6	0.151	0.000199
4	90	142.3	135.8	0.158	0.000249
5	90	141.7	135.6	0.136	0.000305
Average		142.4	136.5	0.154	
+/-		0.5	1.3	0.018	

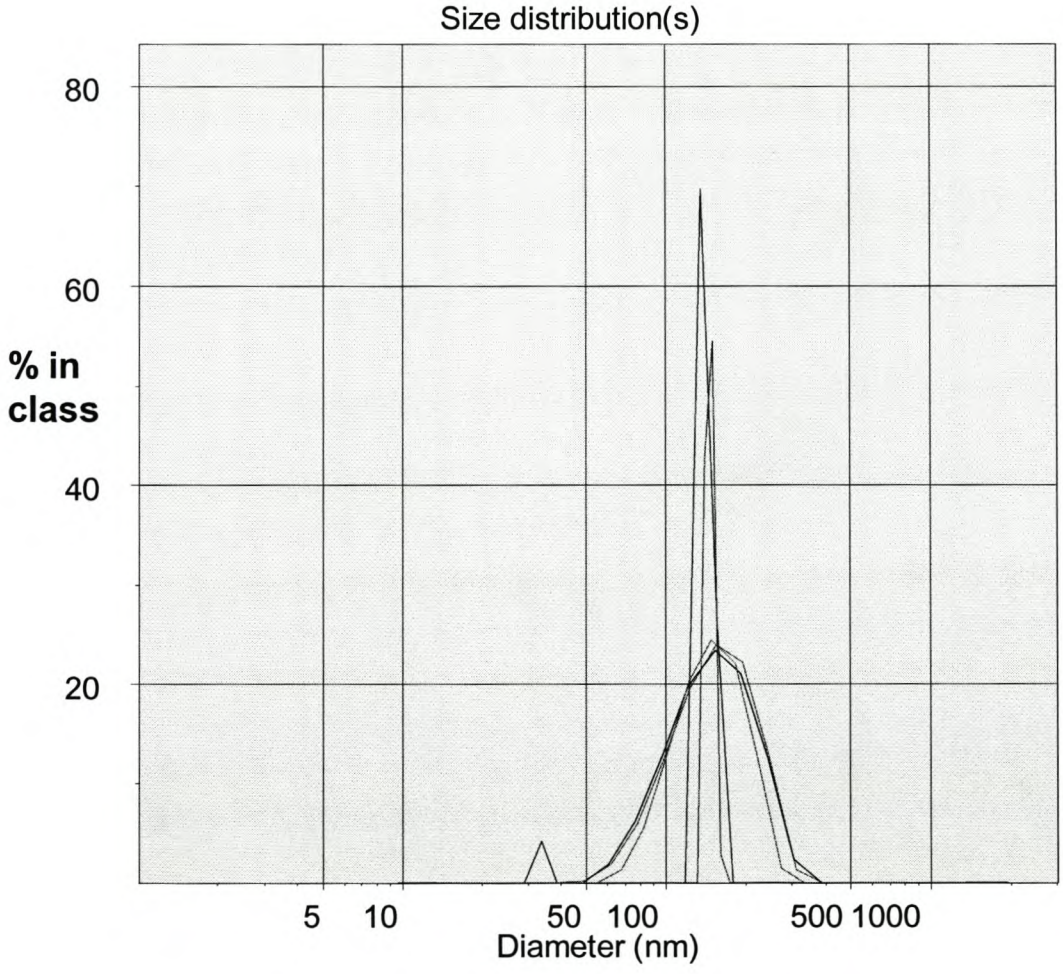


Figure 6.15: Particle size distribution of 4% LMA-grafted phosphated PU prepared via urethane synthesis method 2

Run	Angle	KCps.	ZAve	Poly	Fit
1	90	155.5	136.2	0.079	0.000286
2	90	155.9	131.4	0.104	0.000269
3	90	155.9	130.5	0.095	0.000436
4	90	155.2	130.8	0.086	0.000249
5	90	155.4	129.5	0.080	0.000243
Average		155.6	131.7	0.089	
+/-		0.3	2.6	0.011	

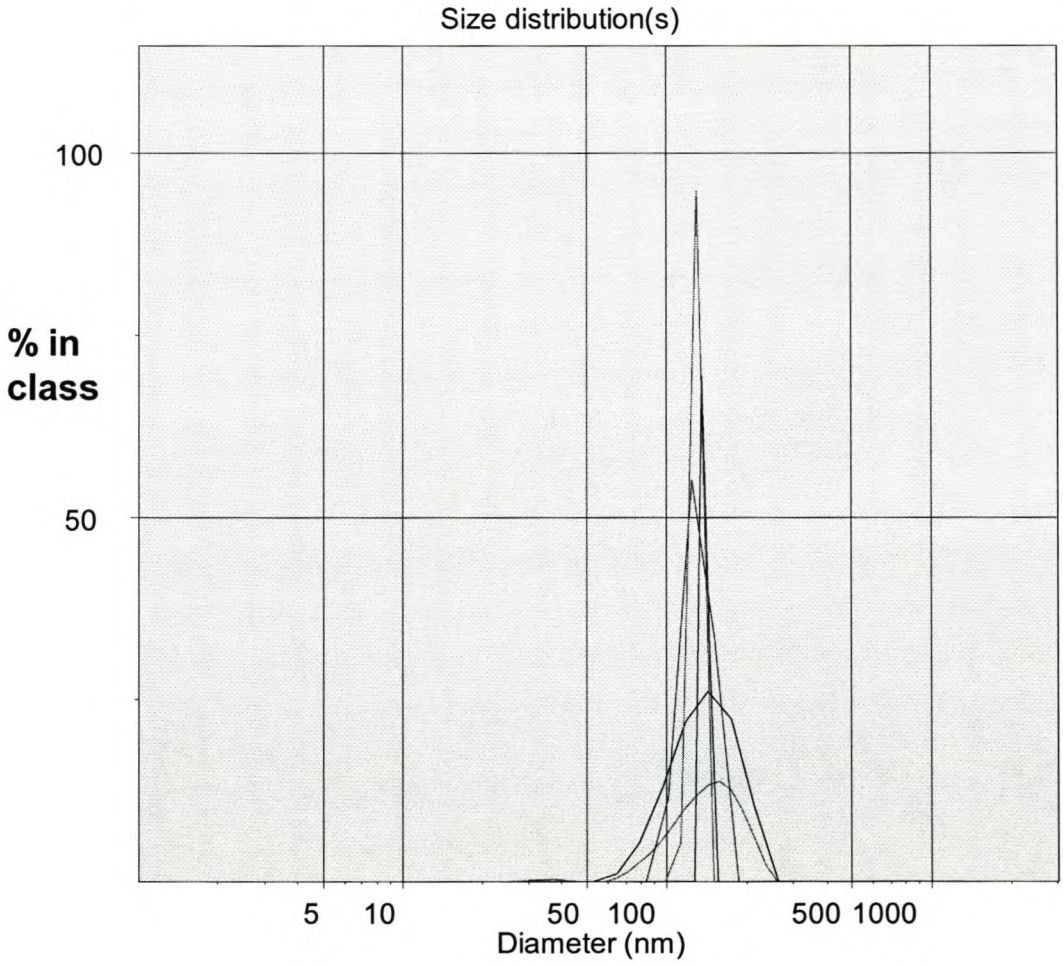


Figure 6.16: Particle size distribution of 8% LMA-grafted phosphated PU prepared via urethane synthesis method 2

Run	Angle	KCps.	ZAve	Poly	Fit
1	90	112.4	158.9	0.075	0.000306
2	90	112.7	156.5	0.105	0.000314
3	90	112.5	157.3	0.107	0.000453
4	90	112.3	156.9	0.087	0.000387
5	90	112.2	155.9	0.085	0.000377
Average		112.4	157.1	0.092	
+/-		0.2	1.1	0.014	

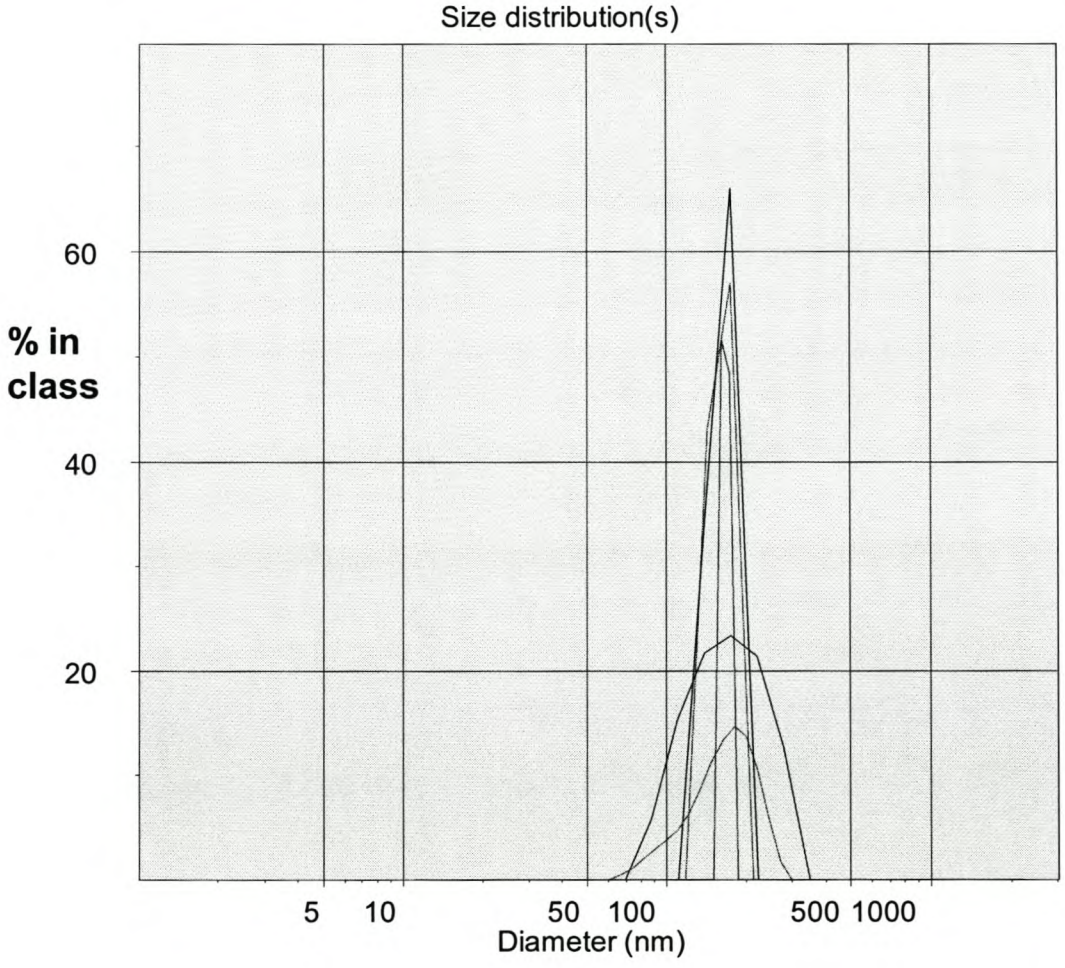


Figure 6.17: Particle size distribution of 12% LMA-grafted phosphated PU prepared via urethane synthesis method 2.

Run	Angle	KCps.	ZAve	Poly	Fit
1	90	115.9	160.1	0.169	0.000231
2	90	116.0	155.2	0.181	0.000190
3	90	116.6	154.2	0.204	0.000313
4	90	116.5	155.5	0.178	0.000297
5	90	116.4	153.3	0.183	0.000230
Average		116.3	155.7	0.183	
+/-		0.3	2.6	0.013	

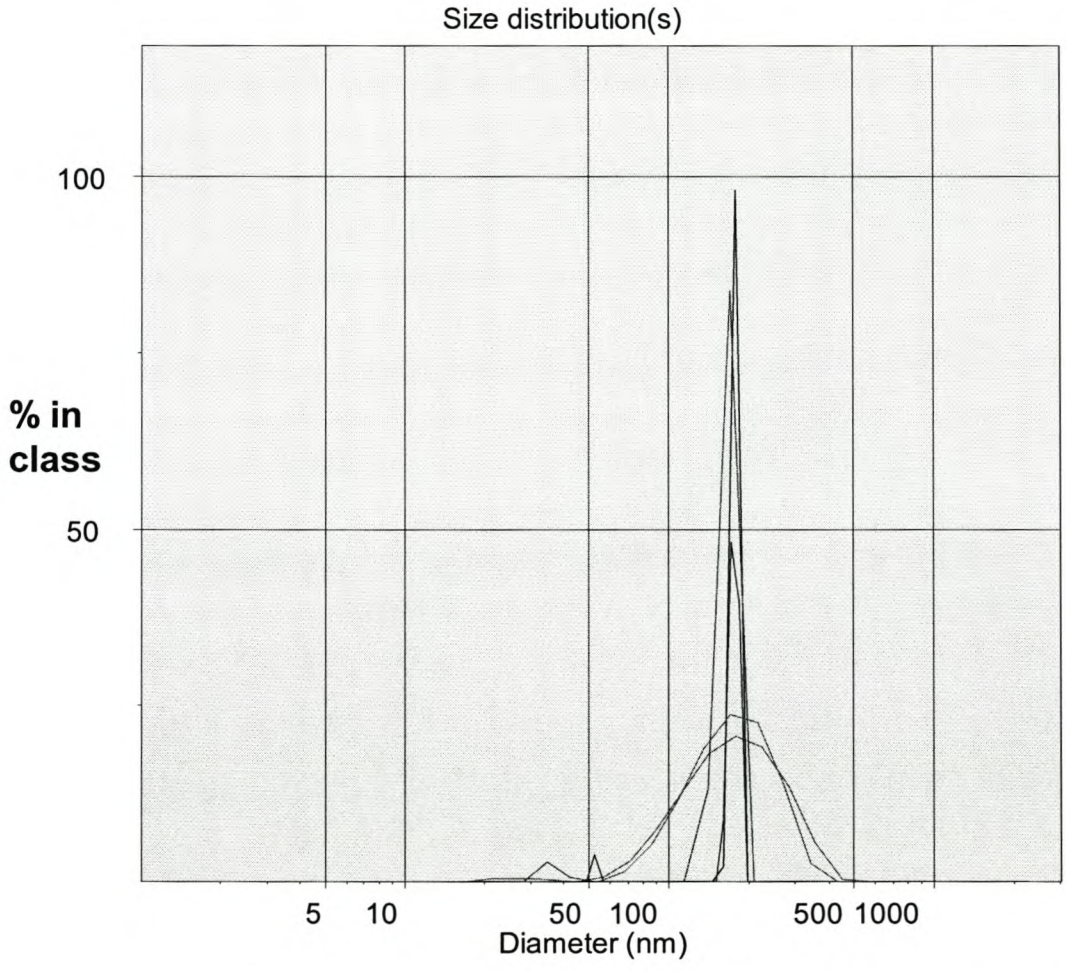


Figure 6.18: Particle size distribution of 16% LMA-grafted phosphated PU prepared via urethane synthesis method 2.

6.4 Scanning Electron Microscopy

Firstly, it was important to see if the coating method had damage the coating surface, and also to look at the surface characteristics. This was done by comparing the obtained SEM images to that in the literature[14-16]. It was concluded that the applied coating method did not damage the coating surface.

6.4.1 SEM images of uncoated paperboard surface

The uncoated paperboard has several holes (pinholes) in between the paper fibers, as seen in Figure 6.19(a) and (b). These pinholes, and the fact that the paperboard has a high affinity for water and water vapor, make it inferior as a water vapor barrier.

6.4.2 Effect of phosphorous on the polyurethane surface

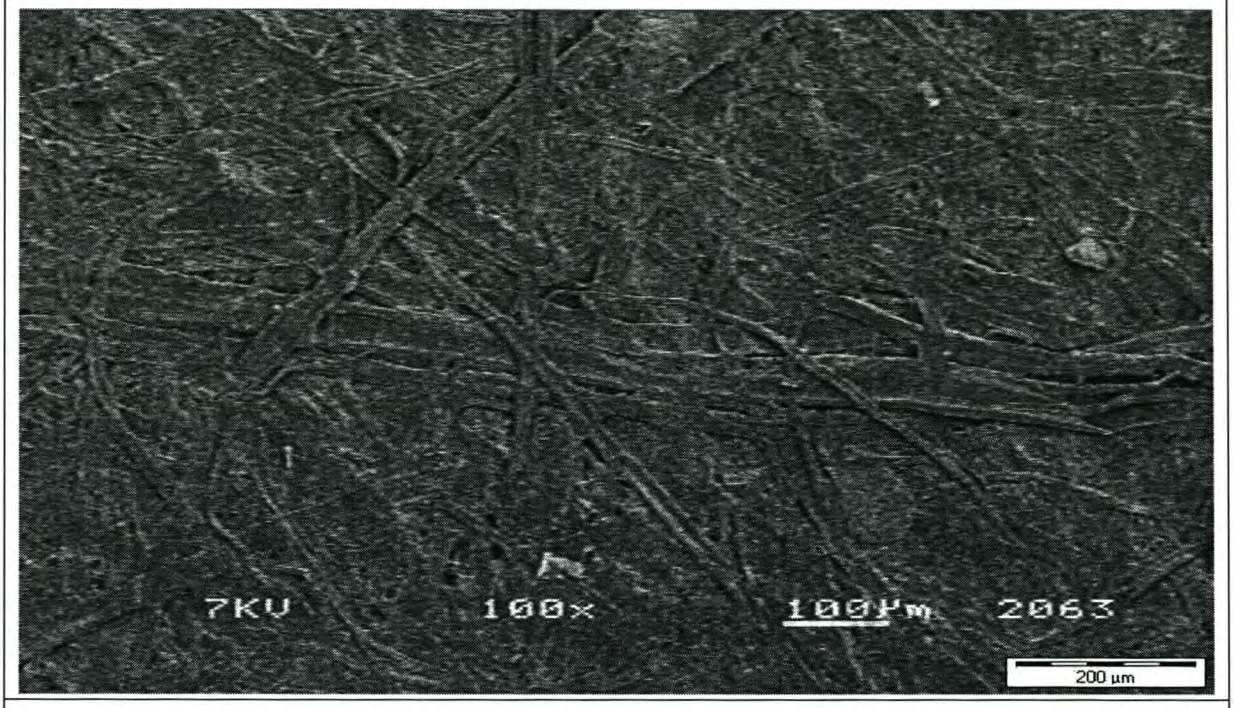
The inclusion of phosphate in the PU-formulation has a clear effect on the SEM-images of the PU-films. When looking at the non-phosphated PU-paperboard samples, we can clearly see that there is still a fair number of pinholes present in the coating (Figure 6.20(a). The addition of wax does lower the MVTR-values considerably, due to its added surface hydrophobicity, but it still does not cover the holes completely (Figures 6.20(b), 6.21(b) and (d), 6.22(b) & 4(d)). The addition of the LMA grafting agent seems to increase the number of holes present in the coating, thereby increasing the MVTR-values (Figures 6.21(a) and (c), 6.22(a) and (c)).

The SEM-images of the phoshated PU-paperboard samples (Figures 6.23-6.28) seem to be totally different from those of the non-phosphated PU samples (Figures 6.21 and 6.22). Firstly, the addition of wax seems to have the same effect as in the case of the non-phosphated PU samples, namely, added surface hydrophobicity and surface smoothness.

6.4.3 Effect of grafting agent on the polyurethane surface

The addition of grafting agents seems to affect the SEM-images considerably. At 0-8% grafting, there are no pinholes present, but at 12% grafting, the pinholes are clearly visible (Figures 6.20(c) and (d), 6.23-6.28). This could be due to the bulky phosphate group imparting additional properties such as hydrogen bonding and chain entanglements, resulting in a more interconnecting coating network of hard-and-soft segments. This coating network seems to be stable up to 8% grafting, showing no pinholes. However, it seems to diminish at 12% grafting, leaving some holes unfilled (Figures 6.28 and 6.29).

(a) Blank paper surface at 100x magnification



(b) Blank paper surface at 500x magnification

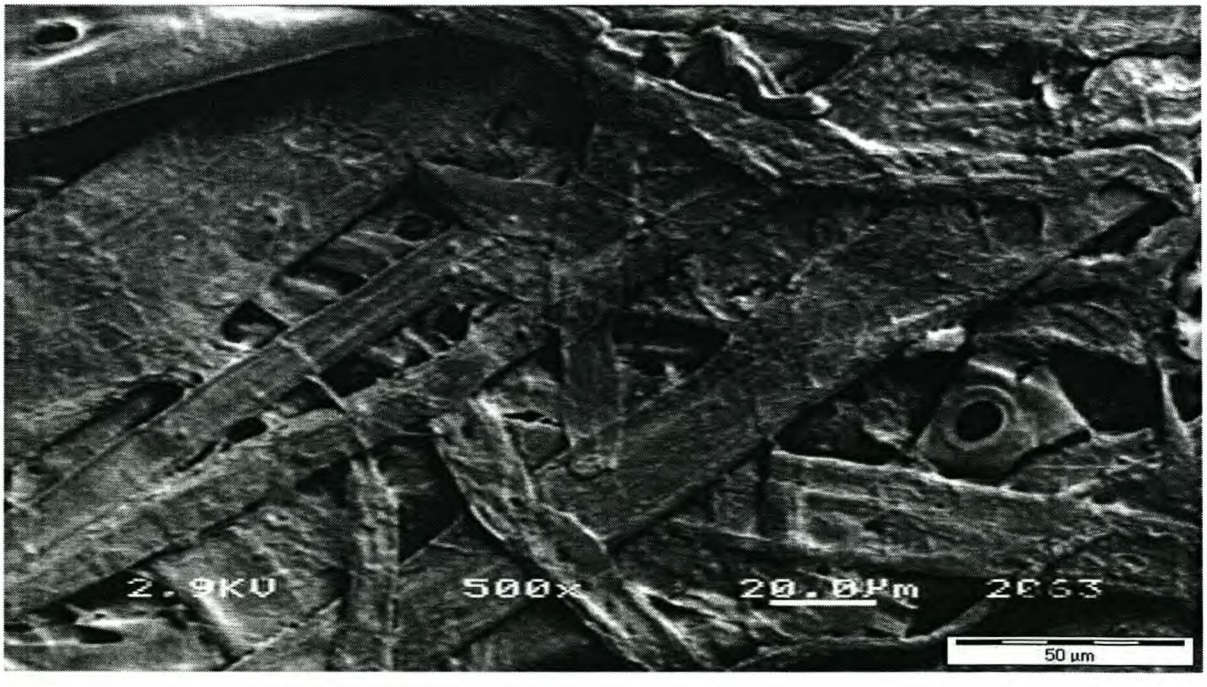
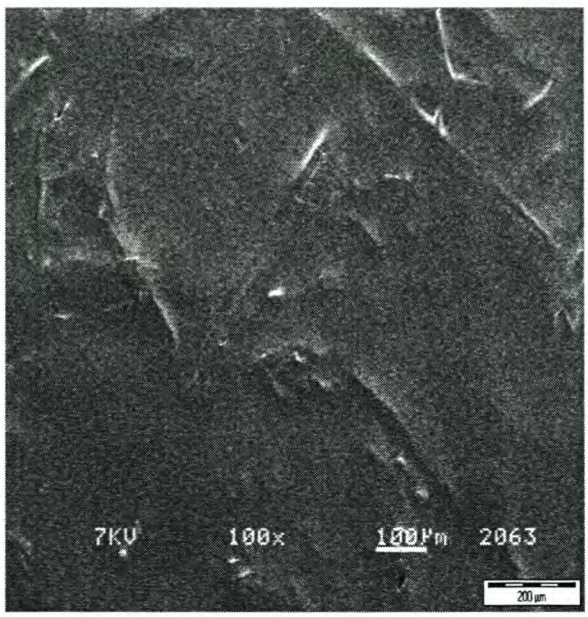
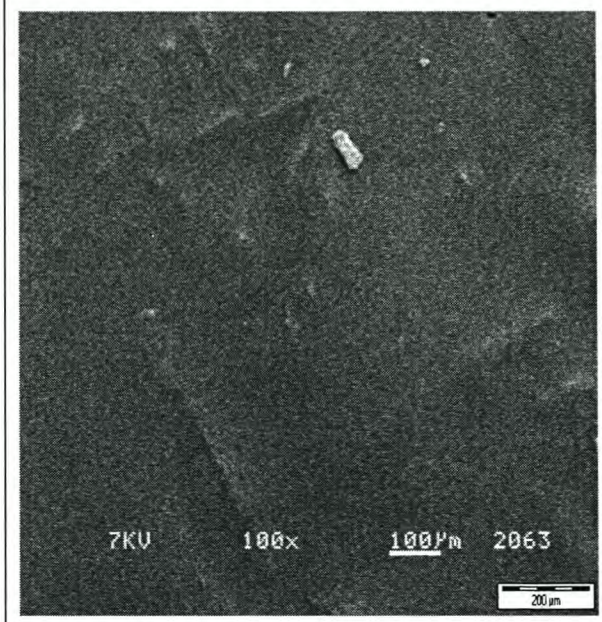


Figure 6.19: SEM-images of the blank paper surface

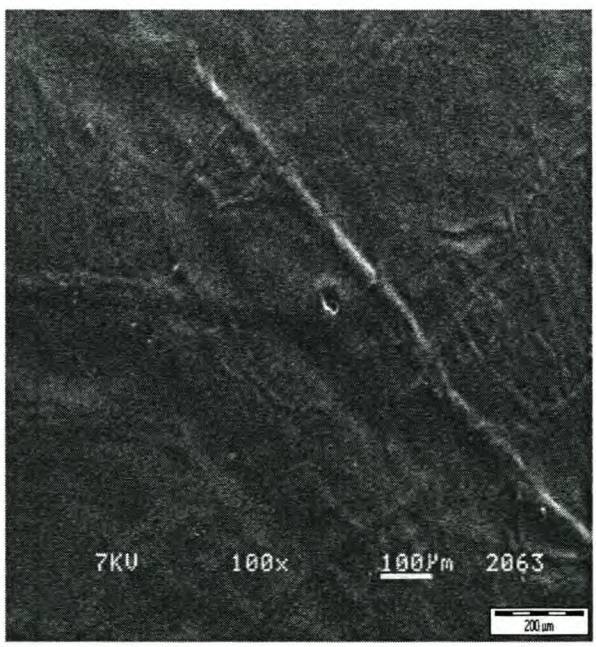
(a) Ungrafted PU with 0% phosphate and 0% wax



(b) Ungrafted PU with 0% phosphate and 15% wax



(c) Ungrafted phosphated-PU with 0% wax



(d) Ungrafted phosphated-PU with 15% wax

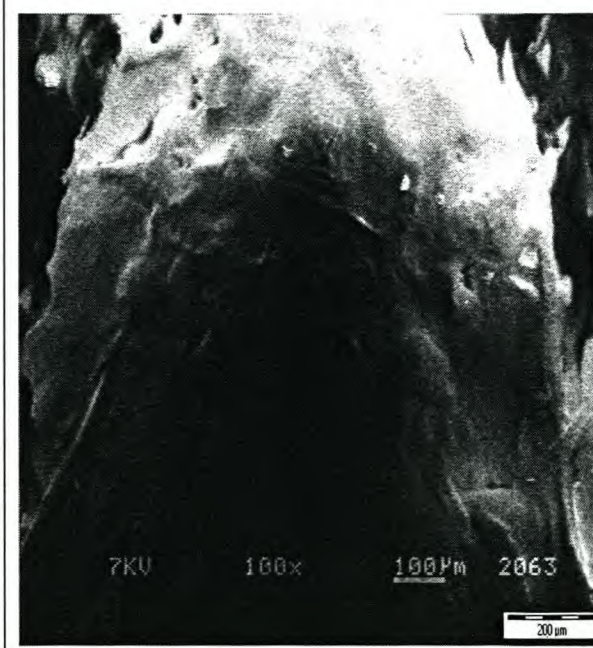
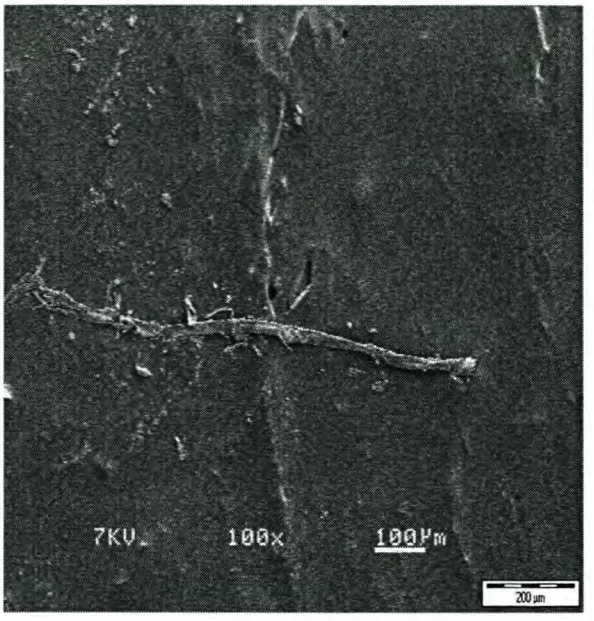
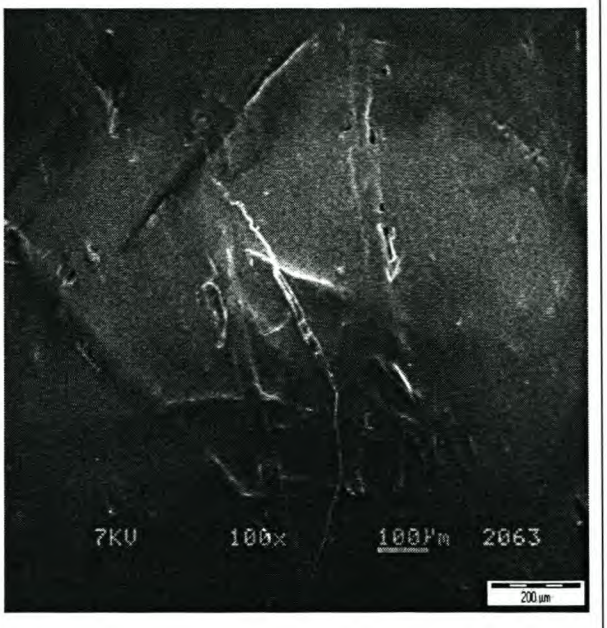


Figure 6.20: SEM images showing the effect of Phosphate on the ungrafted PU coated paperboard

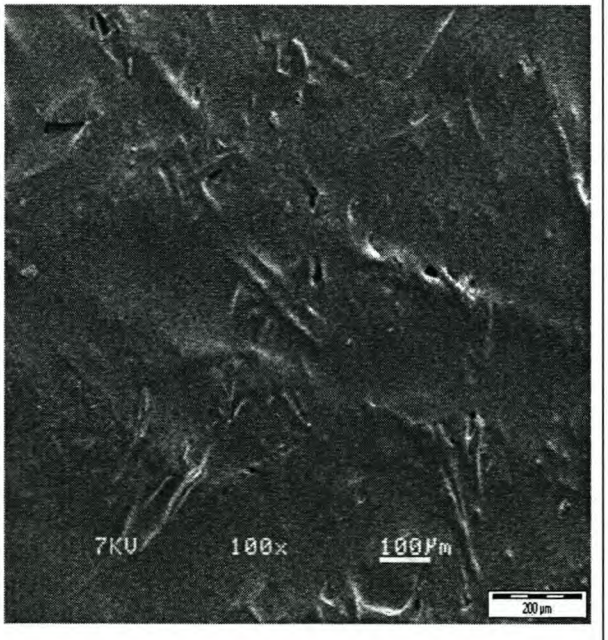
(a) 4% LMA grafted PU with 0% phosphate and 0% Wax



(b) 4% LMA grafted PU with 0% phosphate and 15% Wax



(c) 8% LMA grafted PU with 0% phosphate and 0% Wax



(d) 8% LMA grafted PU with 0% phosphate and 15% Wax

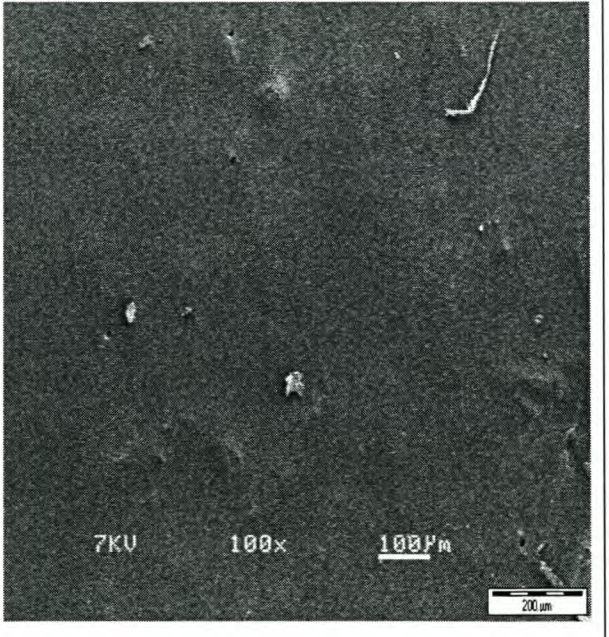
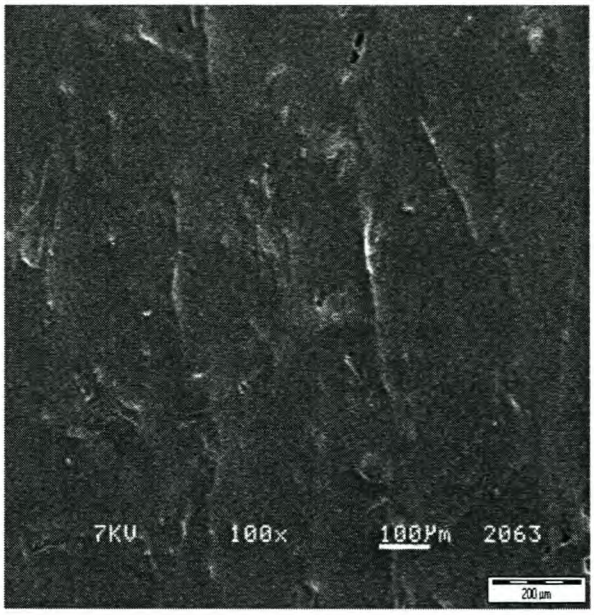
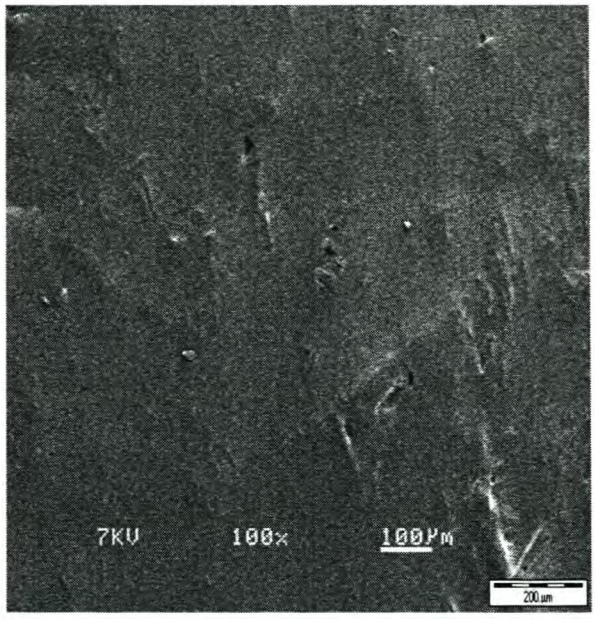


Figure 6.21: SEM images showing the effect of % LMA and % Wax on the non-phosphated PU-2 coated paperboard samples

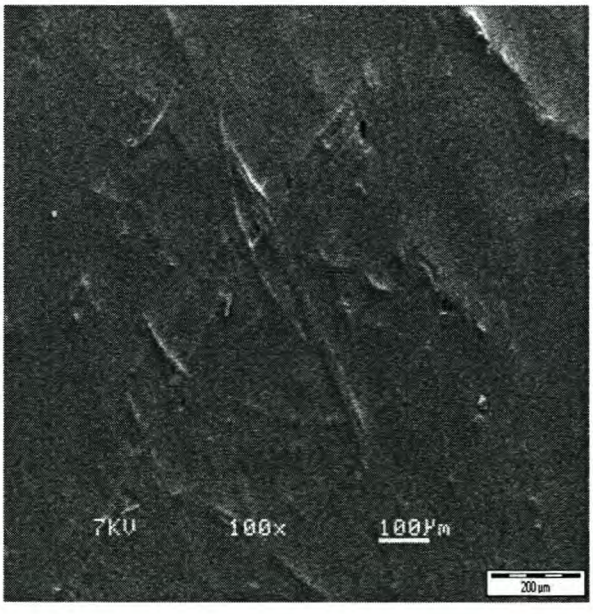
(a) 4% LMA grafted PU with 0% phosphate and 0% Wax



(b) 4% LMA grafted PU with 0% phosphate and 15% Wax



(c) 8% LMA grafted PU with 0% phosphate and 0% Wax



(d) 8% LMA grafted PU with 0% phosphate and 15% Wax

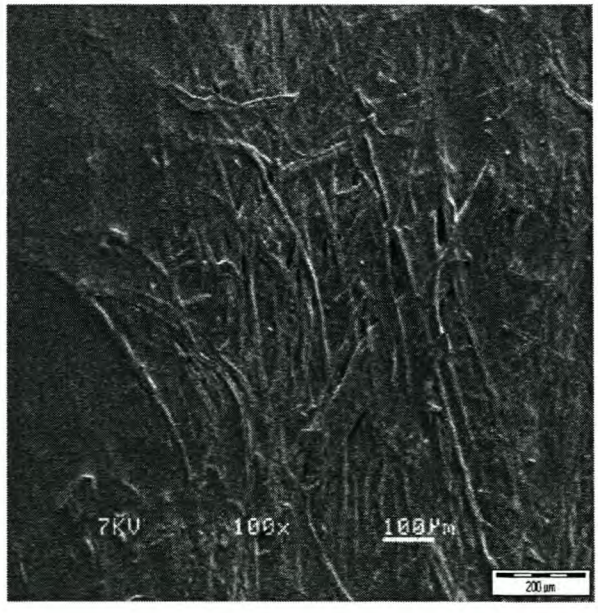
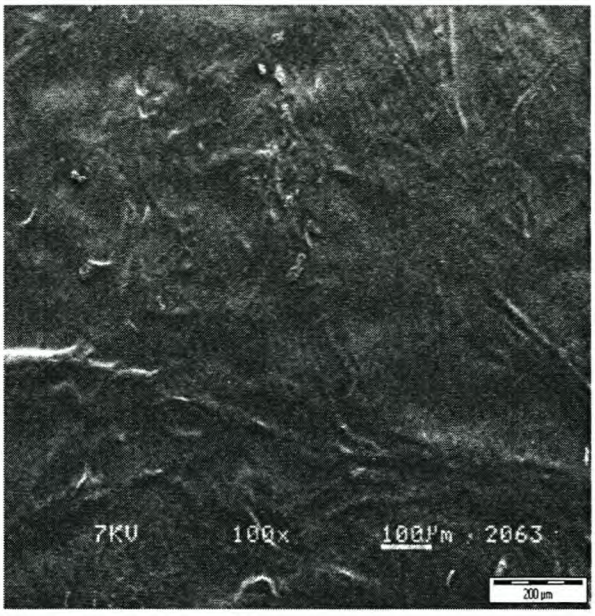
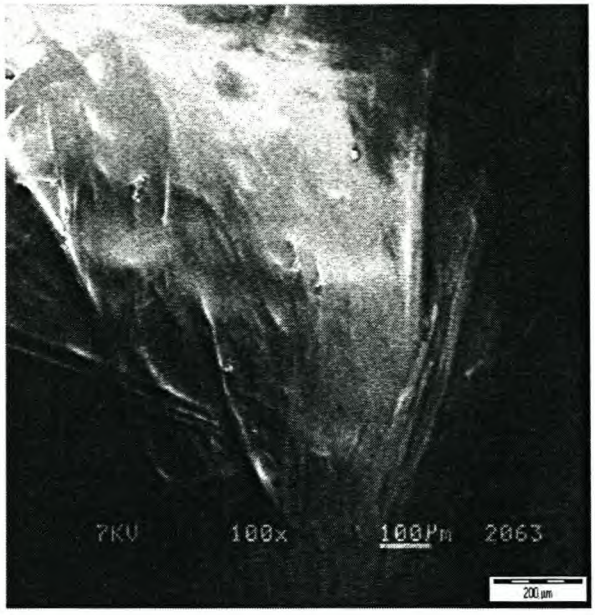


Figure 6.22: SEM images showing the effect of % LMA and % Wax on the non-phosphated PU-5 samples

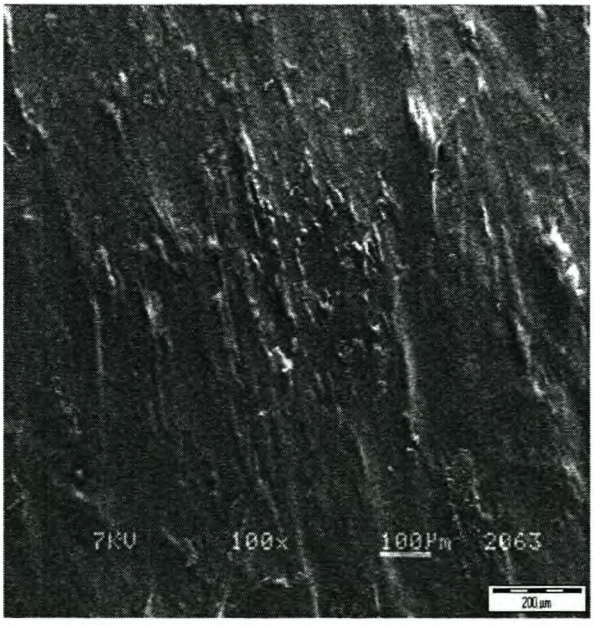
(a) 4% MMA-grafted phosphated PU with 0% Wax



(b) 4% MMA-grafted phosphated PU with 15% Wax



(c) 8% MMA-grafted phosphated PU with 0% Wax



(d) 8% MMA-grafted phosphated PU with 15% Wax

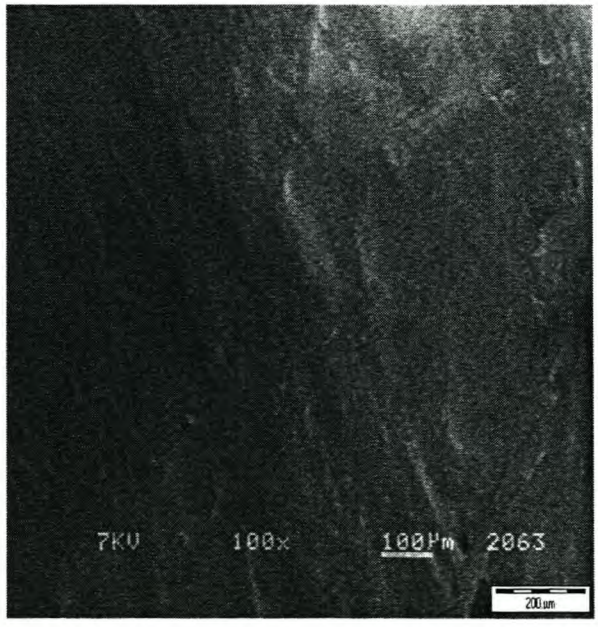
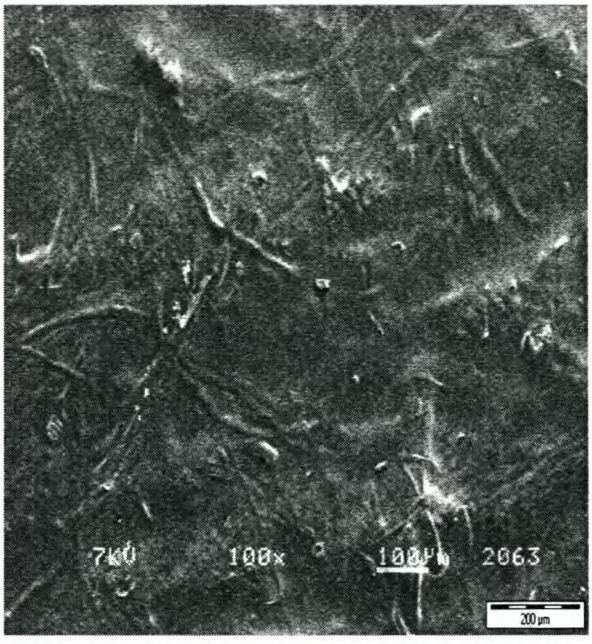
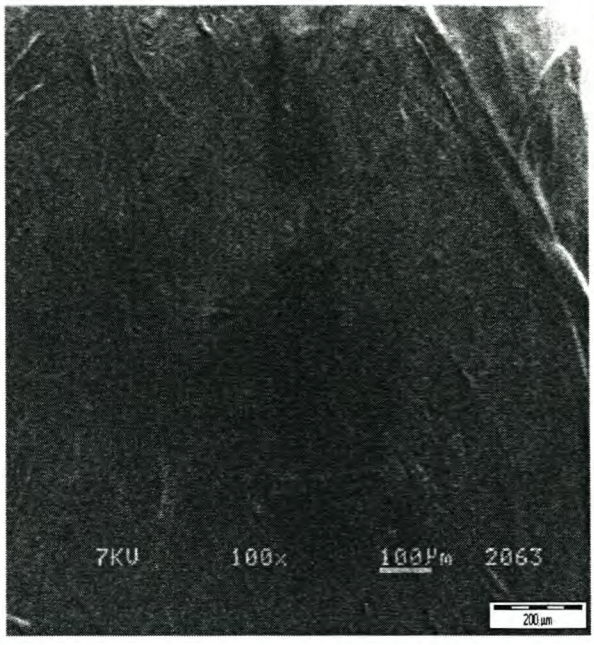


Figure 6.23: SEM images showing the effect of % MMA and % Wax on the phosphated PU-9 coated paperboard

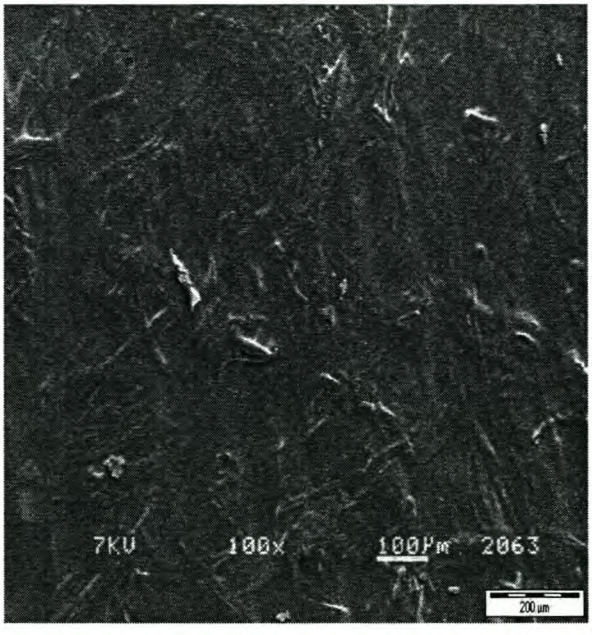
(a) 4% n-BMA-grafted phosphated PU with 0% Wax



(b) 4% n-BMA-grafted phosphated PU with 15% Wax



(c) 8% n-BMA-grafted phosphated PU with 0% Wax



(d) 8% n-BMA-grafted phosphated PU with 15% Wax

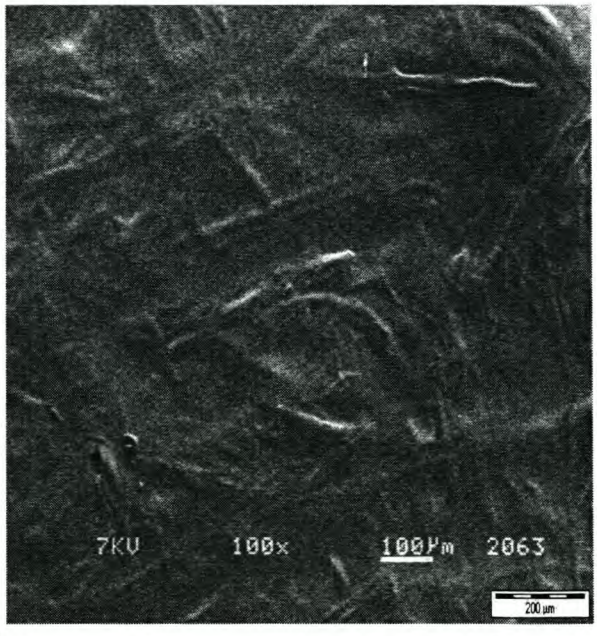
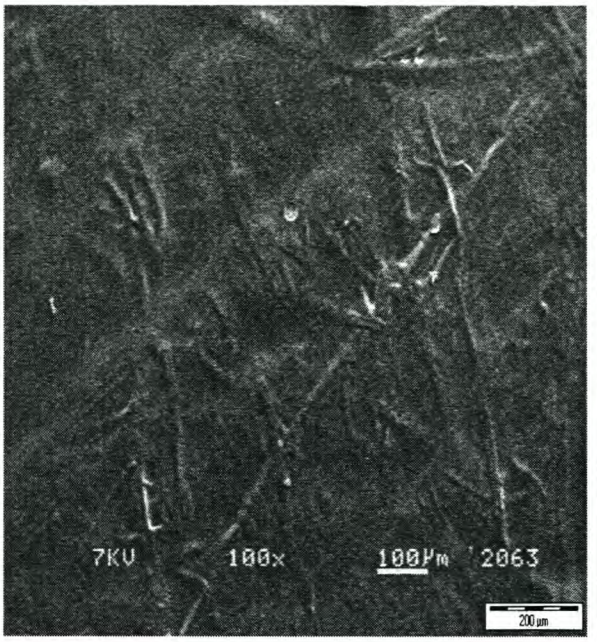
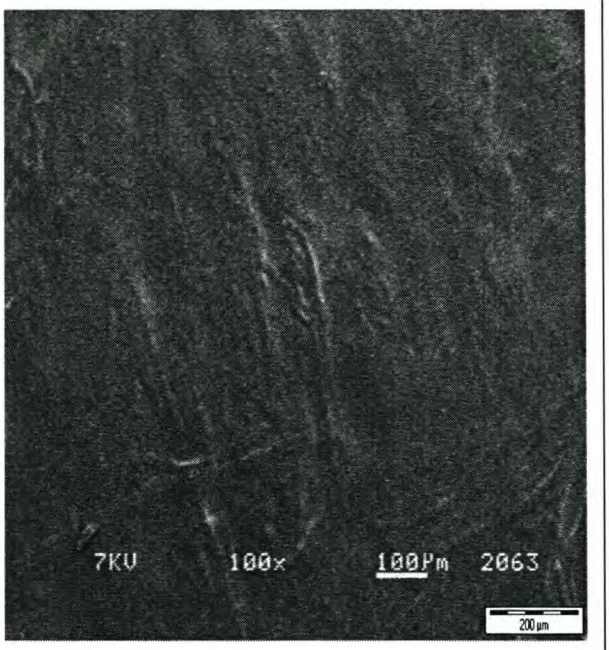


Figure 6.24: SEM images showing the effect of % n-BMA and % Wax on the phosphated PU-8 coated paperboard

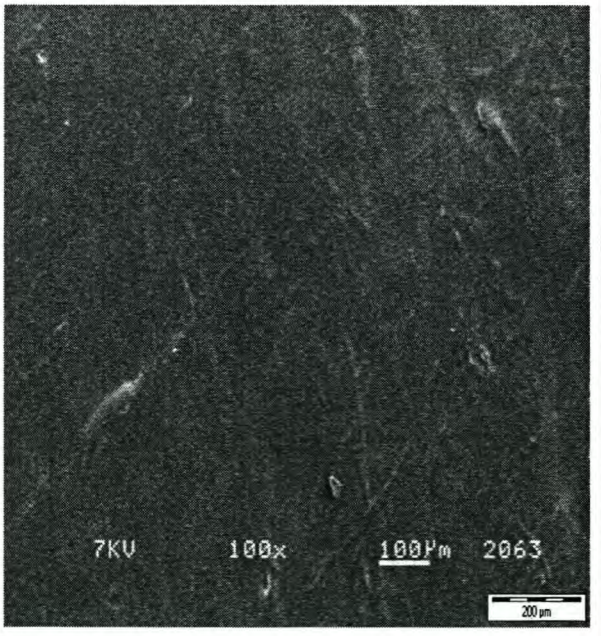
(a) 4% LMA-grafted phosphated PU with 0% Wax



(b) 4% LMA-grafted phosphated PU with 15% Wax



(c) 8% LMA-grafted phosphated PU with 0% Wax



(d) 8% LMA-grafted phosphated PU with 15% Wax

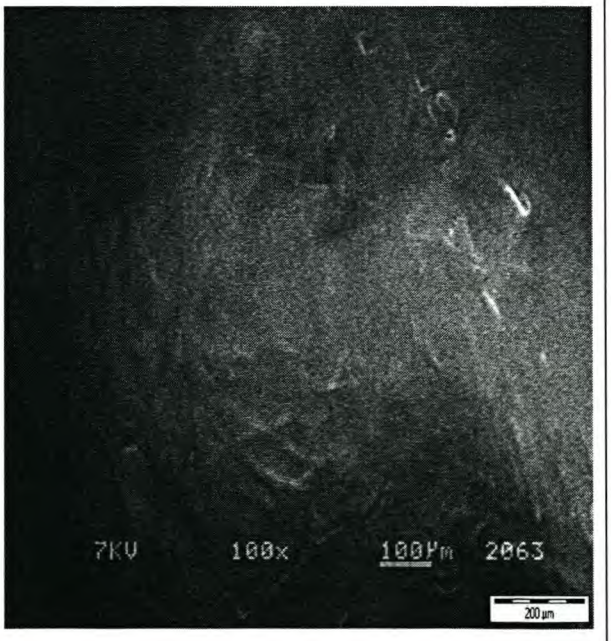
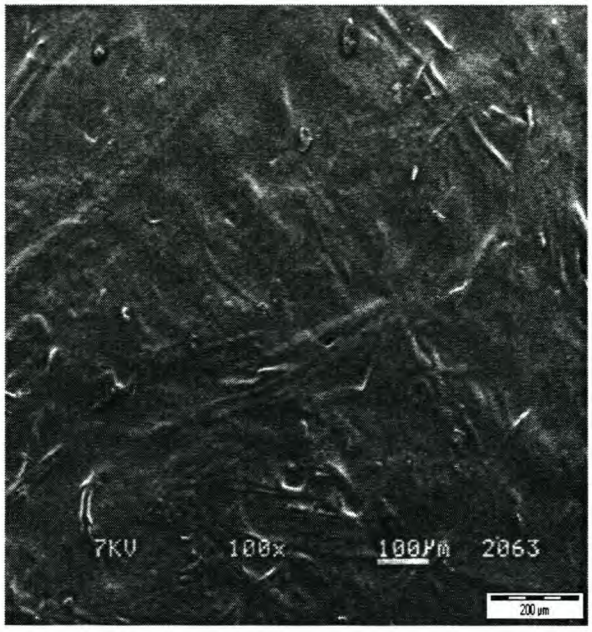
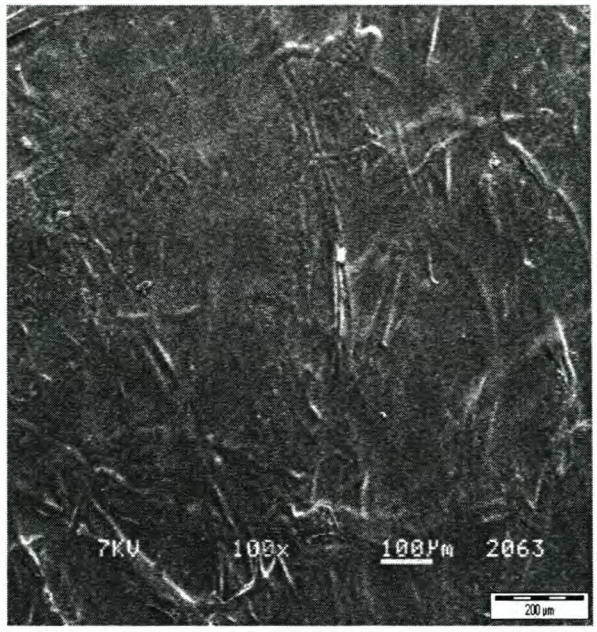


Figure 6.25: SEM images showing the effect of % LMA and % Wax on the phosphated PU-7 coated paperboard

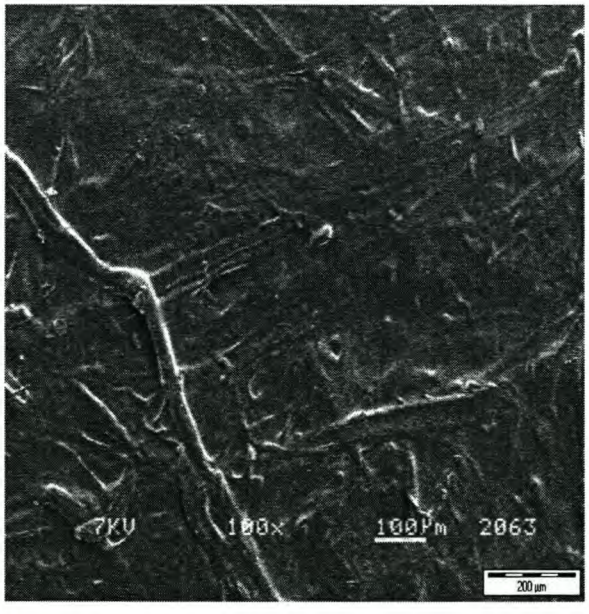
(a) 4% Styrene-grafted phosphated PU with 0% Wax



(b) 4% Styrene-grafted phosphated PU with 15% Wax



(c) 8% Styrene-grafted phosphated PU with 0% Wax



(d) 8% Styrene-grafted phosphated PU with 15% Wax

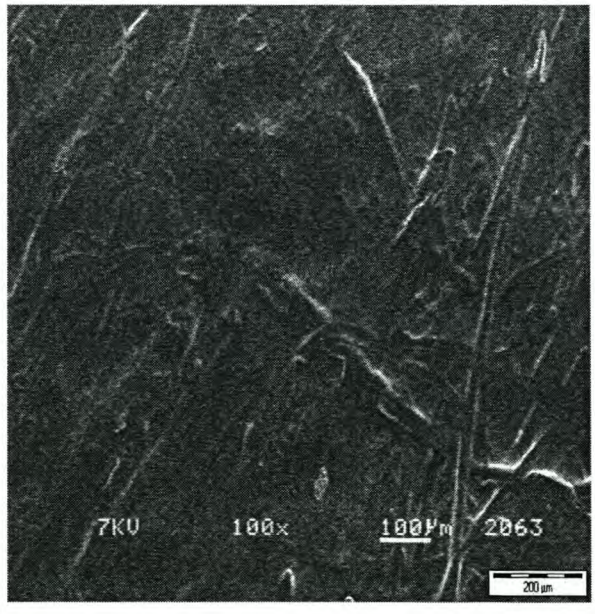
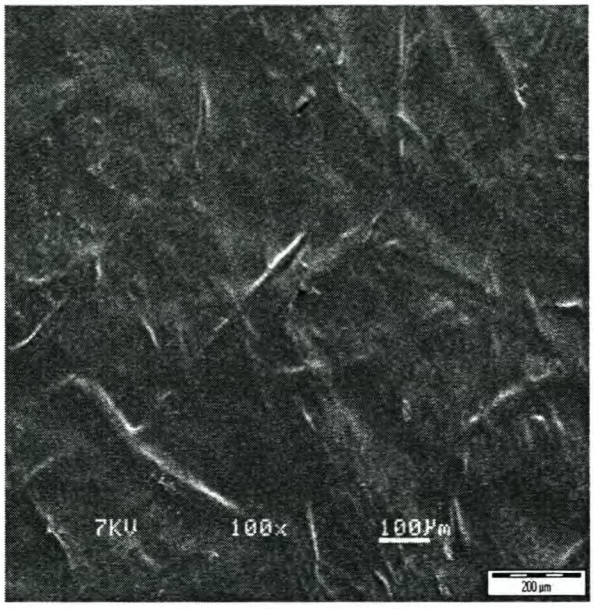
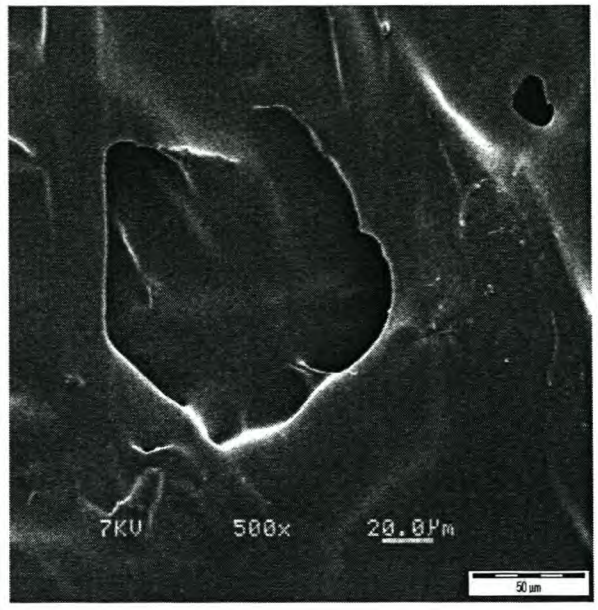


Figure 6.26: SEM images showing the effect of % Styrene and % Wax on the phosphated PU-10 coated paperboard

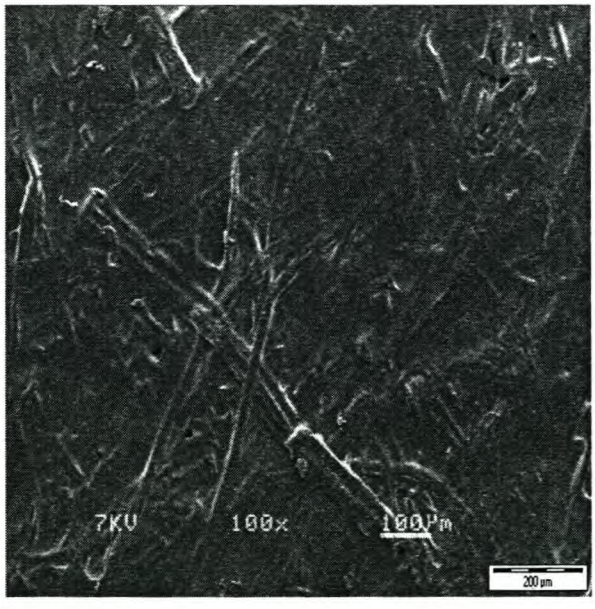
(a) 12% MMA-grafted phosphated PU with 0% Wax, at 100x magnification



(b) 12% MMA-grafted phosphated PU with 0% Wax, at 500x magnification



(c) 12% n-BMA-grafted phosphated PU with 0% Wax, at 100x magnification



(d) 12% n-BMA-grafted phosphated PU with 0% Wax, at 500x magnification

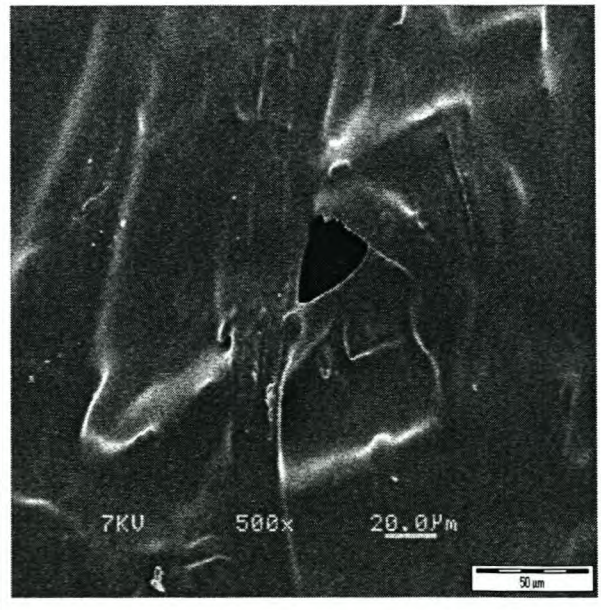
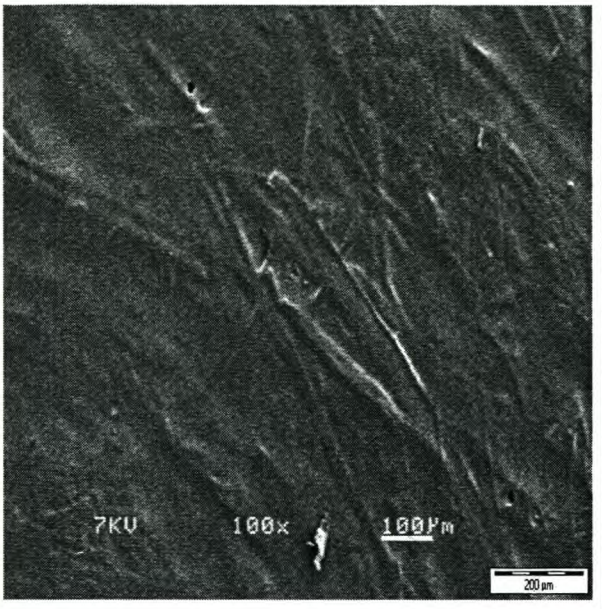
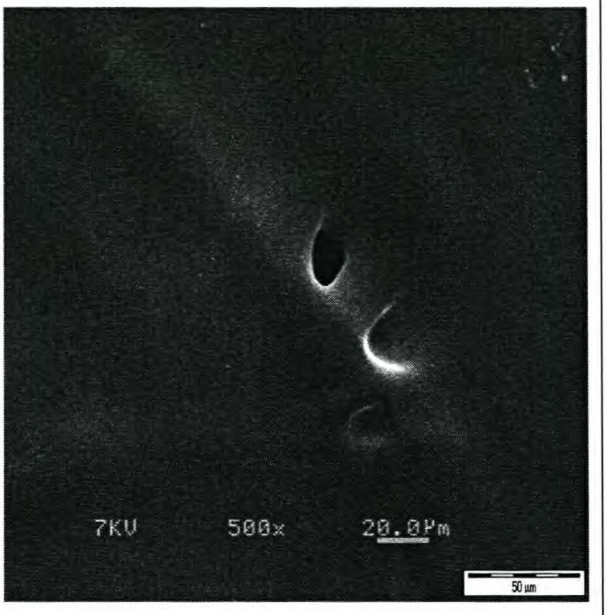


Figure 6.27: SEM images showing the effect of 12% MMA and 12% n-BMA on the phosphated PU coated paperboard

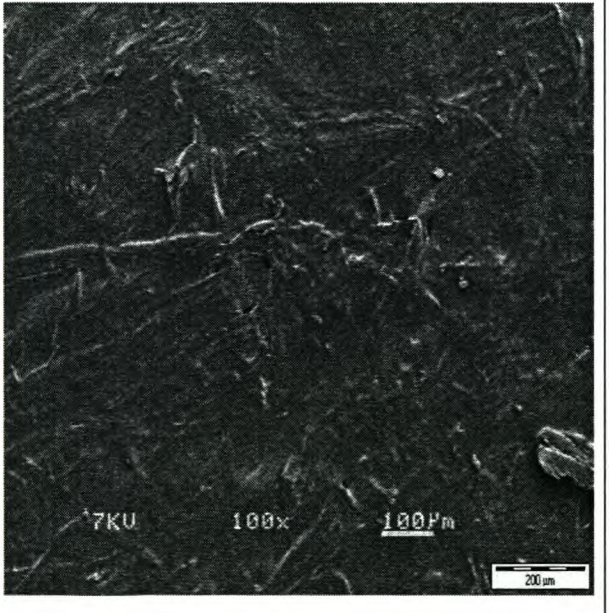
(a) 12% LMA-grafted phosphated PU with 0% Wax, at 100x magnification



(b) 12% LMA-grafted phosphated PU with 0% Wax, at 500x magnification



(c) 12% Styrene-grafted phosphated PU with 0% Wax, at 100x magnification



(d) 12% Styrene-grafted phosphated PU with 0% Wax, at 500x magnification

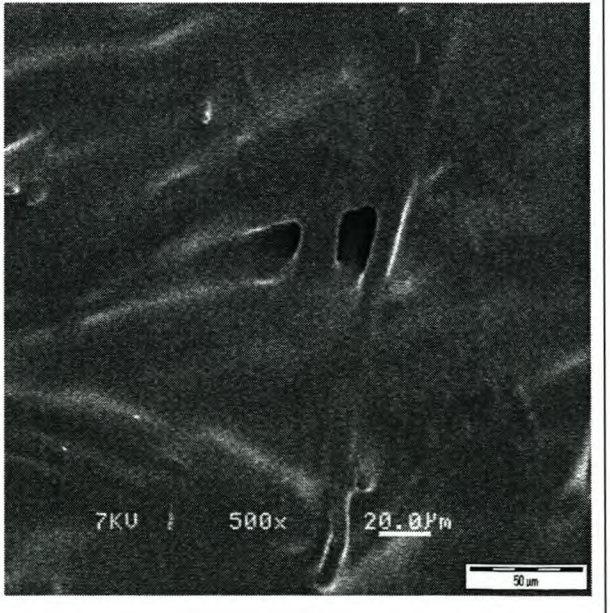
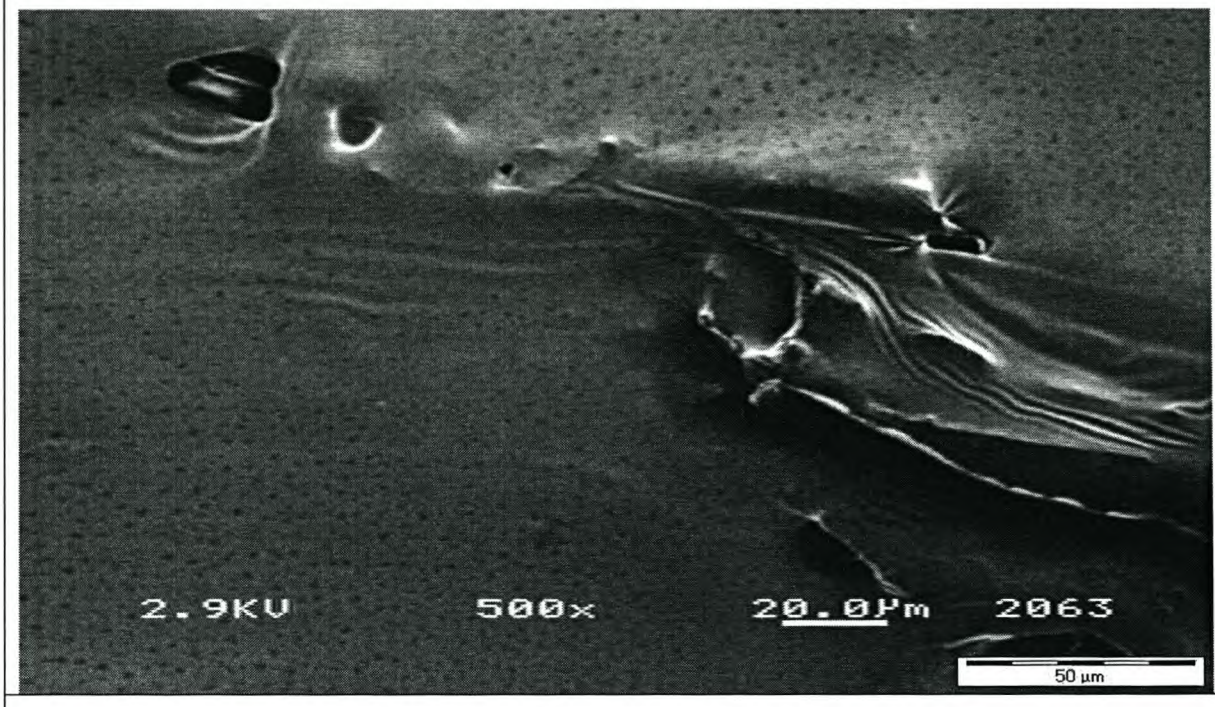


Figure 6.28: SEM images showing the effect of 12% LMA and 12% Styrene on the phosphated PU coated paperboard

(a) 4% LMA grafted-PU with 0% phosphate and 0% Wax at 500x magnification



(b) 4% LMA-grafted phosphated PU with 0% Wax at 500x magnification

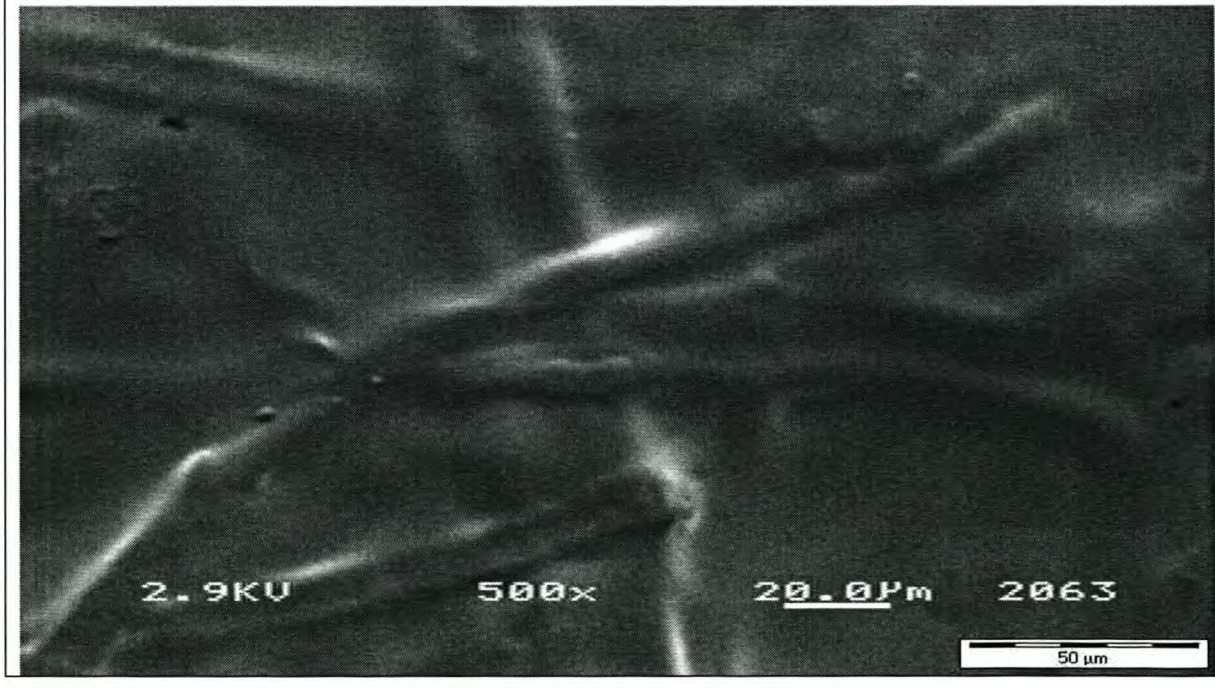


Figure 6.29: SEM images showing the effect of Phosphate on the PU coated paperboard at 500x magnification

6.7 Moisture Vapour Transmission Rate

The composition of the PU-formulation has a definite effect on the MVTRs obtained from the different coated paperboard disks.

6.7.1 Effect of phosphate on the polyurethane

The inclusion of phosphate in the PU-formulation, has an effect on the MVTR-values of the PU-films. The MVTR-values of the non-phosphated PU-paperboard samples are generally higher than those of the phosphated PU samples. See Tables 6.2 and 6.3.

6.7.2 Effect of grafting agent on the polyurethane

The addition of all grafting agents seems to affect the MVTR-values of the phosphate containing PUs considerably more than those of the non-phosphate-containing PU. See Table 6.2 and 6.3.

During the application of the coatings onto the paperboard, it was noted that coatings containing more than 10% grafting agent produced circular patches on the coated paperboard surface. The size of these circular patches seemed to be affected by the amount and the polarity of the grafting agent. An increase in the amount of grafting agent used increased the circular patches. Similarly, a decrease in the polarity of the grafting agents, which is from MMA to n-BMA to LMA, also increased the circular patches on the coated paperboard surface. These coatings also had considerably higher MVTR-values. This could be due to the emulsion particles becoming larger and unstable with increasing amount of grafting agent.

6.7.3 Effect of Semi-crystalline wax on the polyurethane

Different waxes affect the MVTR-values differently, as is seen from results of a preliminary test performed, as seen in Appendixes 3 to 5. From these tests, the two waxes, wax A15/31 and wax C78 seemed to be most useful. This is probably due to their lower acid values, semi-crystallinity and high molecular masses. Thus, the addition of the latter two waxes lowered the MVTR-values considerably, as expected, due to their added surface hydrophobicity and compatibility with the soft segment of the polyurethane.

6.7.4 Conclusions

The lower MVTR-values obtained from the phosphate-containing PUs, is probably due to the phosphate leading to an increasing in the compatible between the soft-and-hard segments (see 6.2), thereby increasing the moisture barrier properties of the coating.

The MVTR-data obtained from the different grafted non-phosphated PU are summarized in the following Table 6.2.

Table 6.2: MVTR Results of the non-phosphated PUs

Non phosphated PU sample	% Grafting	$MVTR_{ave}$ with 0% Wax	$MVTR_{ave}$ with 15% Wax A15/31	$MVTR_{ave}$ improvement with 15% Wax A15/31 (%)	$MVTR_{ave}$ with 15% Wax C78	$MVTR_{ave}$ improvement with 15% Wax C78 (%)
PU-1	0	723	333	53.9	x	x
	6.9	741	245	66.9	x	x
	10	753	342	54.6	x	x
	12	785	378	51.8	x	x
	15	779	460	40.9	x	x
	20	779	505	35.2	x	x
PU-2	0	745	242	67.5	237	68.2
	1	789	287	63.6	300	62.0
	2	775	269	65.3	373	51.9
	3	761	249	67.3	361	52.6
	4	787	287	63.5	380	51.7
	5	782	283	63.8	360	54.0
	6	785	297	62.2	296	62.3
PU-4	0	794	370	53.4	x	x
	2	747	331	55.7	x	x
	4	786	431	45.2	x	x
	6	793	396	50.1	x	x
	8	748	335	55.2	x	x
	10	785	523	33.4	x	x
	12	813	458	43.7	x	x
PU-5	0	743	558	24.9	294	60.4
	2	745	626	16.0	338	54.6
	4	788	553	29.8	393	50.1
	6	754	545	27.7	403	46.6
	8	752	587	21.9	344	54.3
	10	730	397	45.6	390	46.6
PU-6	0	814	499	38.7	456	44.0
	2	823	438	46.8	500	39.2
	4	828	483	41.7	569	31.3
	6	821	455	44.6	571	30.5
	8	834	555	33.5	608	27.1
	10	840	574	31.7	624	25.7

PU-3 emulsion was too unstable, while PU-4 became unstable after standing in the cupboard for 3 months, and was thus excluded from the MVTR determination with Wax C78.

The MVTR-data obtained from the different grafted phosphated PU on paperboard are summarized in the following Table 6.3.

Table 6.3: MVTR Results of the phosphated PU

Grafting agent	% Grafting	$MVTR_{ave}$ with 0% Wax	$MVTR_{ave}$ with 15% Wax A15/31	$MVTR_{ave}$ improvement with wax A15/31 addition (%)	$MVTR_{ave}$ with 15% Wax C78	$MVTR_{ave}$ improvement with wax C78 addition (%)
LMA	0	517	240	53.6	126	75.6
(PU-7)	4	543	228	58.0	142	73.8
	8	560	340	39.3	184	67.1
	12	580	375	35.3	170	70.7
	16	609	378	37.9	241	60.4
n-BMA	0	517	240	53.6	126	75.6
(PU-8)	4	608	158	74.0	197	67.6
	8	616	207	66.4	204	66.9
	12	739	241	67.4	262	64.5
MMA	0	517	240	53.6	126	75.6
(PU-9)	4	632	174	72.5	150	76.3
	8	643	184	71.4	183	71.5
	12	651	235	63.9	290	55.5
	16	674	237	64.8		
Styrene	0	517	240	53.6	126	75.6
(PU-10)	4	590	200	66.1	247	58.1
	8	736	198	73.1	340	53.8
	12	725	278	61.7	379	47.7

6.8 Blocking Test

This characteristic is imperative in the paperboard industry, as blocking results in a coated paperboard, when stacked in pallets, sticking to each other, and damaging the coating (see Appendix 7 for the blocking test method used to determine whether coated sheets in a pallet will stick to each other).

The inclusion of phosphate reduces blocking of the dry coating considerably, compared to the non-phosphate containing coating, as seen in Table 6.5 below.

Table 6.5: Blocking results of the PU coated paperboard samples

	Non phoshated PU paperboard coatings	**Phoshated PU paperboard coatings**
a) Without wax	Medium	Kissing
b) With 15% wax A15/31	Kissing	Kissing (much less than (a))
c) With 15% wax C78	Kissing (less than (b))	None

6.9 References

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7 CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

I. Poly(neopentyl-adipate) macrodiol was synthesized by polycondensation process to an acid value of 3 mg/g of KOH and a hydroxyl-value of 76 mg/g of KOH. A second macrodiol was synthesized using adipic acid, neopentyl glycol 1,4-cyclohexane dicarboxylic acid and phoshonobutane tricarboxylic acid. This macrodiol had an acid-value of 6 mg/g of KOH and a hydroxyl-value of 306 mg/g of KOH.

II. Both synthesized macrodiols were used in the synthesis of segmented polyurethanes. The urethane hard segment consisted H_{12}MDI, DMPA, HPA and HEMA. The role of the DMPA/HPA was to provide the polyurethane with enough ionic centers for dispersion in water. An increase in ionic content decreased the particle size of the polyurethane dispersion, and it also increased the stability of the dispersion.

III. LMA, n-BMA, MMA and styrene were successfully grafted onto the polyurethane via the HEMA spacer using potassium persulphate as an initiator.

IV. The phosphorous containing urethanes had a significant effect on the coating properties of the paperboard. The non-phosphate-containing urethane coated paperboard had a much stickier feel, compared to the phosphate-containing PU coated paperboard. The stickiness (blocking) is an important factor in the coating of paperboard, which should be none, otherwise the piles of stacked paperboard would stick to each other. The MVTR-values of the phosphated polyurethane coatings were also lower than that of the non-phosphated polyurethane coatings.

IV. The grafted polymers had an impact on the MVTR-values of the coated paperboard samples. It was found that the optimum amount of grafting agent used is 5% (of the total amount of solids), and that the maximum amount of grafting agent should not exceed 10% (of the total amount of solids). Above 10% grafting agent, the coatings produced circular patches on the paperboard surface, thereby increasing the MVTR-values.

V. PU/wax-composites were prepared by adding 15% wax emulsion into the polyurethane emulsion prior to being coated onto the paperboard. These composites gave much lower MVTR-values compared to that without any wax, and also decreased the stickiness of the coatings. The two waxes that were used are wax A15/31 and wax C78. Wax C78 seemed to give better results than wax A15/31 in terms of MVTRs. The amount of wax (15%) used in the formulation did not cause a problem to machinery and the paperboard when the coated paperboard was recycled (see Appendix 9) and it is also acceptable in industry.

7.2 Recommendations for Future work

- To improve the desired properties obtained from the synthesized phosphated PU, especially in terms of the cost. Some ideas include substituting the phosphate monomer with a cheaper polar monomer and using a cheaper aromatic isocyanate like TDI or MDI.
- To increase the versatility of the PU polymer in the paper coating industry, e.g. incorporating printability as a characteristic.

8 APPENDICES

Appendix 1:

Polyester Polyol Synthesis Procedure

Experimental setup

A 1-litre glass reactor vessel equipped with a reflux condenser, thermocouple, heating mantle, temperature control unit, mechanical stirrer, N_2-gas, Dean-Starke trap, and Teflon seals and gaskets were used in the polyester polyol synthesis.

Experimental procedure

- Charge the reactor vessel with raw materials.
- Increase the temperature to 100°C, under slow agitation, until all the raw materials have melted.
- Raise the temperature to 120°C at a maximum heating rate of 1°C/min, while purging with N_2-gas. This slow heating rate is required to minimize glycol and phosphoric acid loss.
- Increase the temperature to 210-230°C at a maximum heating rate of 1°C/min. The stirrer speed should be adjusted to 300-350 rpm after 50% of the calculated water has been removed.
- If any glycol is lost, it can be adjusted for by adding the lost amount of glycol at this stage of the reaction.
- As the reaction nears its end-point, add xylene to help remove water through aziotropic distillation from the reaction mixture, and increase the stirrer speed to 400-450 rpm. The amount of xylene needed should be adjusted to obtain a good reflux.
- Monitor the reaction progress by measuring the acid value by acid-base titration.
- The reaction should take about 12 hours to reach completion, after which the reaction mixture is cooled down to 80°C.
- The polyester polyol is then dried and degassed under vacuum for 48 hours to remove any water traces prior to being used.

Appendix 2:

Polyurethane Synthesis Procedure

Experimental setup

A 1-litre glass reactor vessel was used in the PU synthesis, equipped with a reflux condenser, thermocouple, heating mantle, temperature control unit, Teflon seals and gaskets, mechanical stirrer, and N_2-gas.

Experimental procedure

- Before charging the reactor, make sure that the raw materials are free of any moisture traces.
- Charge the reactor vessel with DMPA, H_{12}MDI and MEK-solvent (40-50% of the total MEK-solvent amount to be added). Make sure that the reaction is continuously purged with N_2-gas and that it is properly sealed.
- Increase temperature to 75-85°C at 150-200 rpm until 30-60 minutes after the DMPA has dissolved.
- Pre-mix the polyester macrodiol with the rest of the MEK-solvent, and then add it to the reaction mixture. Continue the reaction for 2 hours at 75-85°C at 200-250 rpm.
- Decrease the temperature to 50-60°C, and add HEMA and HPA monomer and DBTL catalyst. The reaction is continued for 2-3 hours at 55-60°C.
- When no NCO-peaks are present as measured by FTIR, reduce the reaction temperature to 50°C and add the neutralizing agent. Let the reaction continue for 45-60 minutes. At a temperature of 45-50°C, add the grafting agent and let the reaction continue for 1.5-2 hours.
- At a temperature of 40°C, add water while the stirrer speed is increased to a minimum of 500 rpm. This is done to take the polymer from the solvent medium into the water medium, which acquires a high rpm.
- Remove the solvent via vacuum or a rotary vapour at 40°C.
- At a temperature of 40°C, add water while the stirrer speed is increased to a minimum of 500 rpm. This is done to take the polymer from the solvent medium into the water medium, which acquires a high rpm.
- Remove the solvent via vacuum or a rotary vapour at 40°C.

Appendix 4:

Polyurethane-Wax Composites[1]

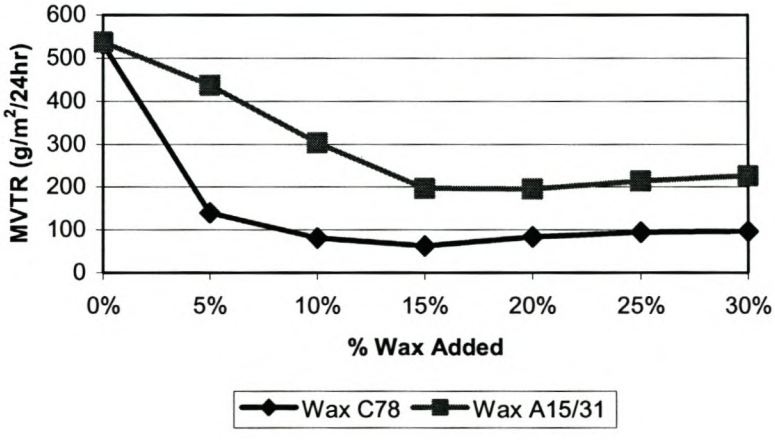
Experimental layout:

The emulsion composites of Wax A15/31 with PRP urethane and Wax C78 with PRP urethane were tested under tropical conditions, i.e. 38°C and 90% RH, for a period of 24 hours.

Emulsion coatings:	PRP urethane (26.5% total solids content)
	Wax 5 (25.9% total solids content)
	Wax C78 (25.9% total solids content)
Wax concentrations (mass %):	0%, 5%, 10%, 15%, 20%, 25% and 30%
Curing:	110°C for 10 minutes

Results

The results are depicted below.



From the above graph, it was concluded that the addition of 15% wax to the PU emulsion resulted in a minimum MVTR.

Appendix 5:

Wax Properties

Properties	Wax C78	Wax A15/31
Colour	White liquid	Amber liquid
Odour	Waxy	Waxy
Density at 20°C	0.98 g/cm^3	0.98 g/cm^3
Boiling point (bp)	100°C (water)	100°C (water)
Solubility in water (20°C)	Dilutable	Dilutable
Flash point (°C)	Approx. 189	Approx. 230
	(After evaporation of water)	(After evaporation of water)
pH-value, aqueous extract	9.7	10.9
Physical state	Liquid	Liquid
Viscosity @ 30°C (cP)	45	4
Explosion properties	None	None

Appendix 6:

MVTR Test Method

This method is based on the MVTR test as developed by Mondi Cartonboard division.

Purpose:

Moisture Vapour Transmission Rate (MVTR) test is done to determine the amount of moisture vapour that will pass through a board in 24 hours at specified conditions of relative humidity and temperature.

Apparatus:

- Humidity cabinet set at 38°C and 90% relative humidity.
- Moisture resistant vessel of 84 mm diameter, open at the top and equipped with a screw-on open lid with a rubber seal.
- A balance, accurate to two decimal places.
- Silica gel with a colour indicator.

Test Procedure:

- Dry silica gel in oven for 2 hours at 110°C.
- Add 100 g silica gel to the bottom of the vessel.
- Cut a round disc sample and fit in the lid of the vessel.
- Screw the lid with the sample onto the vessel.
- Weigh the vessel on the balance and record the weight (A) to two decimals.
- Leave the sample in the humidity cabinet for 24 hours at 38°C and 90% relative humidity.
- Re-weigh the vessel after 24 hours and record the weight (B).
- Calculate the open area of the vessel in m^2.
- Calculate the MVTR by means of the following equation:

$$MVTR_{24} = \frac{B - A}{Area}$$

MVTR: Moisture Vapour Transmission Rate ($g/m^2/24h$)

A: Weight of jar prior to 24h exposure (in grams)

B: Weight of jar after 24h exposure (in grams)

Area: Area of the circle (m^2)

Appendix 7:

Blocking Test Method

This method is based on the blocking test as developed by Mondi Cartonboard division.

Purpose:
The blocking test is done to determine whether sheets in a pallet will stick to each other if a coating is applied on one or both sides of the sheet.

Apparatus:
A 28 kg weight that applies ±0.5 bar pressure on a surface of the stacked coated paperboards.

Method:
Obtain two samples of coated sheets and apply pressure to them at a consistent pressure of 50 kPa for 24 hours at ±22°C.

If only one side is coated the test can be done either with coating touching coating, or coating touching plain board.

After 24 hours, remove samples from device and carefully pull them apart, notifying the amount of sticking (blocking) occurring.

Report:
Report results as follows:

No sticking:	None
Sticking occurs in only certain areas:	Kissing
Sticking occurs on whole area but no fibre tear:	Medium
Sticking occurs on whole area with fibre tear:	Hard

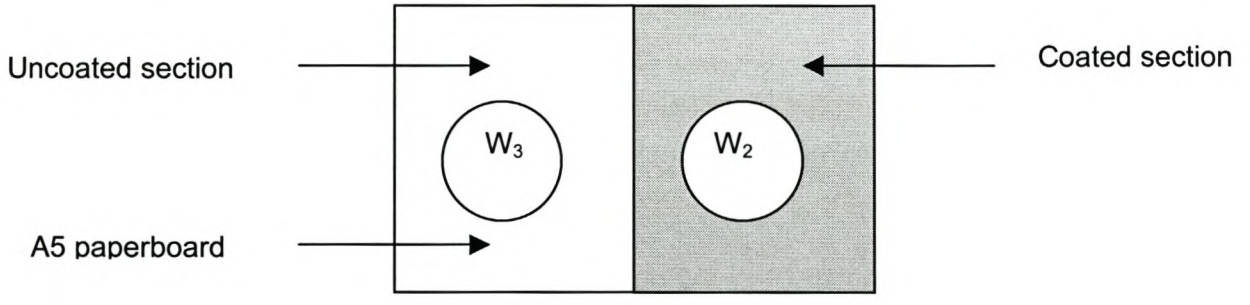
Appendix 8:

Coating weight determination[1]

The A5 paperboard is coated halfway (see Figure below) with an emulsion coating and cured in an oven at 110°C for 10 minutes. Thereafter two circles (with 84 mm diameter) are punched out, representing the uncoated and the coated sections of the paperboard. Both the uncoated and the coated circles are heated at 110°C for 30 minutes and weighed while still hot. (W_2 and W_3) (See Figure below). The dry coating weight is then calculated by means of the following equation:

$$\text{Coating} = \frac{(W_2 - W_3)}{\text{Area}}$$

Coating:	Dry weight of coating applied (g/m^2)
W_2:	Weight of coated circle (in grams)
W_3:	Weight of uncoated circle (in grams)
Area:	Area of circle (m^2)



Appendix 9:

Recyclability Evaluation[1]

A. Recyclability Methodology

Paper Pulping

Purpose: To break up the paperboard into a fine pulp.

Approximately 400 grams of paperboard is required for the current recyclability process used. The paperboard is shredded by hand and soaked in water before being pulped. It is then placed into a 25-litre container, half filled with water. An overhead stirrer, equipped with a shredder is used, to pulp the paperboard. A low speed setting is used for the initial 15 minutes, whereafter it is set at the high speed setting and left for 30 minutes to pulp the paperboard. The quality of the paper pulp is tested by taking a small amount (spatula tip) of the pulp and dispersing it in a beaker of water. The completion of the pulping process is indicated by the absence of solid paperboard particles. Only the individual fibres should be visible.

Screening Test

Purpose: To separate the paper fibres from the coating and other additives.

A slit screening machine (a ±25 litre-capacity cylinder with an interchangeable slit screen bottom) with 0.1mmx50mm slits, is used to separate the fibres from other constituents in the coated paperboard. Constant water pressures in conjunction with a blender-type-mixing blade are used to ensure separation of the fibres by forcing the paper pulp fibres through the slits. The water is then guided through a sieve, with a mesh size smaller than the pulp fibre, in order to accumulate the raw fibre. The pulp fibre is collected and placed in a bag that allows water drainage. It is then put in an industrial spinning machine to get rid of excess water. The pulp fibre is later used in the making of the hand paper. The residue (everything too big to go through the slits) is then dried, weighed and expressed as a percentage waste solid to pulp fibre.

$$\%\ \text{Waste Solid} = \frac{\text{Residue}}{\text{Fibre pulp}} \times 100$$

The consistency (solid content) of the fibres is then determined as follows:

- A small sample of the spin-dried fibre is placed in a glass beaker and weighed
- The beaker with fibre sample is placed in an oven to dry

$$\text{Consistency} = \frac{\text{Weight(after)}}{\text{Weight (before)}} x100$$

- After 48 hours the beaker is weighed again to determine the dry weight of the fibre
- The consistency of the fibres is required to accurately weigh off 42g of fibre for the handpaper-making process.

Handpaper

42g of fibre is required for the handpaper-making process. This is accurately weighed off by using the consistency as determined after the screening test.

$$\text{Sample weighed} = \frac{42}{\text{consistency}}$$

Dispersing the fibres

Purpose: To disperse fibres homogeneously in water.

Place the accurately weighed fibre sample into a 1 litre plastic beaker and add sufficient water to break up the fibres with a blender. Use an overhead blender to disintegrate the fibres and disperse it evenly. Place the contents of the beaker into a 20 liter container equipped with an overhead stirrer. Fill the container with 15 litres of water to obtain a 0.28% consistency of the fibres in the water.

Schopper-Riegler Test

Purpose: To determine the Schopper-Riegler (°SR) value of the dispersion

Method 1

Pour 1 litre of dispersed pulp into the Schopper-Riegler-Wert machine and allow the water to drain into the calibrated Schopper-Riegler measuring cylinder. Take the °SR reading from the top of the measuring cylinder. This value is an estimate of the °SR value and can now be verified by means of method 2 below.

Method 2

The Schopper-Riegler-Wert machine is opened up and a disc with paperpulp is removed from it. The remaining water is pressed from it by first placing the paperpulp disc between two layers of cloth and placing it in a small press, followed by placing the paperpulp disc between two sheets of blotting paper and pressing it again between the press. The paperpulp with blotting paper is then placed on a hotplate to dry. The dry disc of paper is

weighed and the weight compared to the Schopper-Riegler chart to determine the accurate °SR value.

Preparation of Handpaper sheets

Ten sheets of handpaper are made to ensure a large enough sample for the testing of the paper afterwards. The procedure for the preparation is as follows:

- Cut 20 pieces of blotting paper (6" x 11.5") and wet it prior to making the handpaper, as each handpaper prepared must be covered on both sides with wet blotting paper
- Half fill the rectangular sheet-former with water (remembering to open the vacuum!)
- Pour 1 litre of dispersed pulp into the rectangular sheet-former
- Fill the rectangular sheet-former up to the mark at the top
- Use the "mixer" to disperse the pulp further in the water (push it down twice)
- Turn the vacuum on and wait for the water to drain completely from the rectangular sheet former
- Lift the top part of the sheet-former and remove the base (which contains the pulp)
- Remove the handpaper from the base by placing a wet sheet of blotting paper onto the paperpulp, followed by 5 dry sheets of blotting paper
- A heavy roller is then moved across the surface of the handpaper (once forward and once backward), to remove excess water
- Remove the dry blotting paper
- Carefully lift the wet blotting paper with the wet paperpulp from the base of the rectangular sheet former
- Place another wet sheet of blotting paper on top, thereby covering the paperpulp between two pieces of blotting paper. This is to ensure that the two sides of the paper exhibit the same physical properties. If this is not done, 2-sided paper is obtained.
- The wet handpaper is then placed on a hotplate to dry

Tests

The handpaper thus made is used to determine its characteristics, to determine the effectiveness of the recycling process. The characteristics are calculated by means of the equations summarised below.

Grammage	$\text{Grammage } (g/m^2) = \frac{\text{Average weight (g) x 10 000}}{\text{Area } (cm^2) \text{ x No. of sheets}}$
Drainage	The drainage is determined during the handpaper making process. This has been described in full in 3.2 above.
Burst Strength	$\text{Burst Index } (kPa.m^2/g) = \frac{\text{Bursting Strength (kPa)}}{\text{Grammage } (g/m^2)}$
Tear Strength	$\text{Tearing Resistance (mN)} = \frac{\text{Average x 16 x 9.807}}{\text{No. of sheets}}$ $\text{Tear Index } (mN.m^2/g) = \frac{\text{Tearing Resistance (mN)}}{\text{Grammage } (g/m^2)}$
Tensile Strength	$\text{Tensile Strength (kN/m)} = \frac{\text{Graph reading from Instron (N)}}{\text{Width of strip (mm)}}$ $\text{Breaking Length (km)} = \frac{\text{Tensil Strength (kN/m) x 102}}{\text{Grammage } (g/m^2)}$

The recyclability tests on the urethane-coated paperboard was done by the Forestry Department, University of Stellenbosch. The recyclability of coated paperboard, with a coating consisting of: PRP urethane, wax 5, mica and amazon clay, was evaluated against the recyclability of uncoated paperboard. The purpose was to determine whether the paperboard, when coated with such coatings, would be recyclable.

B. Experimental Recyclability Evaluation

Sample 1: Uncoated paperboard

Sample 2: Coated paperboard (Blank)

Paper tests	Drainage Tensile strength Tearing resistance Burst strength and burst Index	Tear Index Grammage Breaking length

400 grams of each sample were prepared for the recyclability tests. After the recycling process, the paper pulp was used to make handpaper. These sheets were used for a series

of tests to determine whether the handpaper made from paper pulp from the coated paperboard displayed different characteristics to that of the blank sample.

Results and Discussion

The results are summarised in the Table below.

Recyclability Test Results

Test	Units	Sample 1	Sample 2
Grammage	g/m^2	81.36	78.24
Burst Strength	kPa	110.88	91.38
Burst Index	$kPa.m^2/g$	1.36	1.17
Tearing Resistance	mN	592.78	519.55
Tear Index	$mN.m^2/g$	7.29	6.64
Tensile Strength	kN/m	3.55	3.20
Breaking Length	km	4.45	4.17

These results indicate that the coated paperboard, sample 2, exhibits characteristics very similar to that of the blank sample, sample 1.

The composite evaluated therefore did not significantly influence the recyclability of the paperboard.

8.1 References

1. Valaska Cloete, Paper-Coating Research Group at the Institute for Polymer Science, University of Stellenbosch, part of PhD studies, 2001.